MICROPLASTICS IN SALTMARSHES: DEVELOPING EXTRACTION METHODS AND INVESTIGATING PAST ACCUMULATION.

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Abstract

Saltmarshes are complex, dynamic environments, which play a vital role in protecting both humans and wildlife, by acting as a natural barrier against coastal erosion and flooding, and providing habitats for a diverse range of biota. However, the sources and accumulation of microplastics on saltmarshes have not yet been subject to detailed research. These environments have the potential to resolve the temporal evolution of plastic pollution since production began, and improve understanding of their fate in the coastal environment. The aim of this study is to develop a suitable extraction methodology to investigate temporal trends in the concentration and type of microplastic pollution in saltmarsh sediments, from the mid-20th century to the present day. Two cores were taken from a radionuclide-dated saltmarsh in NW England, in an attempt to evaluate the relationship between microplastic concentrations and sedimentological parameters. A novel method has been developed to optimise the extraction of microplastics from organic rich, fine grained sediments based on sequential density separations with the added benefit of reducing the use of harmful chemicals. The majority of microplastics were separated at a density range of 1.6 - 1.4 g cm^{-3}. Microplastics were found in both cores, with pellets being the most common type, making up 80 % of the total concentration. The record of accumulation observed in both cores taken from Biggar marsh does not follow the growing historical increase in global plastic production. There is no consistent relationship between mean grain size and microplastic concentrations. Future work should focus on improving chronological control to better constrain sedimentation rates to establish microplastic influx over time.

Introduction

Plastic pollution is now an eminent global issue, receiving worldwide attention and calls for action. A reported 9.5 million tonnes of new plastic waste enters the oceans each year (Boucher and Friot, 2017), affecting a vast array of the planet's ecosystems, as well as posing risks to human health (Wright and Kelly, 2017). Since the mass production of plastic began in the 1940's, the amount of plastic produced has increased from 1.5 million tonnes in 1950, to 230 million tonnes in 2009 (Plastics Europe, 2010). Today, plastic is used ubiquitously, yet around 50 % of the plastic produced is thrown away after a single use (Mathalon and Hill, 2014). The increasing demand for the material, as well as the longevity and disposable nature of the product, means this is likely to increase with time (Thompson et al., 2004). The first recorded plastics to become widely used were hard and brittle plastics such as shellac from the late 19th century, and bakelite which was produced mainly from the 1920s to 1940s and is still in minor use today (Zalasiewicz et al., 2016). It was not until the 1940s when plastic production rapidly increased, becoming one of the fastest growing global industries (Gourmelon, 2015). Today, the most common plastics include low-density polyethylene (LDPE), high-density polyethylene (HDPE), polypropylene (PP) and polystyrene (PS) (Andrady, 2011). Due to its long-lasting

nature and low cost, it has become our go-to material for an array of uses, from packaging to clothing, medicine to architecture. However, it is its long-lasting nature that has caused it to become such a wide-spread environmental issue, with both marine and terrestrial environments at risk to its pollution. According to the NOAA, it takes around 450 years for a plastic bottle to decompose in the environment (Fig. 1). On average, we purchase around 38.5 million plastic bottles every single day in the UK, and less than half of this ends up being recycled (House of Commons, Environmental Audit Committee, 2017). There are a number of factors affecting the increase of marine plastic pollution; such as population density and mismanaged plastic waste. Global population increase, and high population densities near the coast (Small and Nicholls, 2003) increases the likelihood of plastic pollution entering marine environments, from direct deposition of plastic litter from recreational areas, beaches and fishing activities, as well as run-off from housing areas and sewage effluent. Many countries do not have effective waste management strategies in place, which increases the probability of plastic debris polluting the environment. Jambeck et al (2015) estimated that 4.8 to 12.7 million tonnes of plastic waste entered the ocean in 2010.

Fig. 1: Estimated decomposition rates of common marine debris items (source: National Oceanic and Atmospheric Administration, U.S.).

Microplastic pollution

Whether plastic is directly deposited onto an area, or if it ends up in the environment indirectly, it will make its way into the marine environment. Here, plastic debris is exposed to a number of physical,

chemical and biological processes which result in the breaking down of larger plastic pieces into much smaller pieces; known as microplastics. There are two main size classifications recognised in the literature for microplastic particles; ≤5mm (Andrady, 2011) and ≤1mm (Claessens et al., 2011). Microplastics can be defined into two types; primary, which are those manufactured to be of microscopic size, and secondary, which result from the break-down of larger plastic debris. These particles are known to have adverse effects on wildlife (Wright et al., 2013), and although the risks to human health are uncertain, it is possible that microplastic pollution will also pose a threat to humans (Wright and Kelly, 2017). The main route of exposure for human populations from contaminants associated with plastic is the migration of contaminants from food packaging into the food itself (Galloway, 2015). Additives are not bound to the polymer matrix and because of their low molecular weight, these substances can leach out of the plastic polymer (Crompton, 2007) into the surrounding environment, including into air, water, food or body tissues.

There are a number of both point and diffuse sources of microplastics, which makes assessing the global distribution trends difficult, with very limited information on the subject (Galgani et al., 2015). Some of the main contributors of microplastics to the environment include fibres from clothing (Napper and Thompson, 2016), car tyres (Kole et al., 2017) and plastic pellets (Boucher and Friot, 2017). Most of these will enter the environment via a number of pathways, such as runoff, sewage outlets or wind. Microplastic pollution has been discovered in an extensive range of environments, from fresh water lakes (Free et al., 2014) and rivers (Hurley, 2018), to the deep sea (Cauwenberghe et al., 2013). The majority of previous research has focused on plastic debris in the marine environment, with studies looking into the effects on marine life such as strangulation, entanglement and ingestion. It has been suggested that by 2050, plastic debris in the ocean will equal, and likely exceed the amount of fish by weight (Jovanovic, 2017). It is widely recognised that due to the proliferation of plastic waste in the marine environment, microplastics in particular are often mistaken for food and ingested by marine organisms. Bioavailability increases with the decrease in size of plastic debris (Gregory, 1996), and microplastics have a greater likelihood of absorbing and desorbing toxic chemicals, due to their increased surface area (Lee et al., 2014). As it stands, knowledge on microplastic pollution in terrestrial environments is limited, despite figures of annual plastic release to land being estimated between 4 – 23 times higher than release to the oceans (Horton et al., 2017).

Plastics in Saltmarshes

With the majority of plastic litter being produced on or near the shore (Thompson, 2017), surprisingly few studies have investigated the presence of microplastic pollution in coastal ecosystems. Environments such as estuaries and tidal flats are very much at risk to microplastic pollution as these are the transitional pathways from terrestrial to marine ecosystems. One of the most important

transitional environments are saltmarshes. These are unique, dynamic ecosystems, formed by the accumulation of sediment in low energy environments, where tidal currents and wind-wave action are limited (Foster et al., 2013). There are a number of processes influencing the source of sediment available for deposition onto the marsh; for example, sediment load is more likely to be deposited when the rate of water flow onto the marsh is reduced, which is usually caused by the presence of vegetation (Boorman et al., 1998).

Saltmarshes play a vital role in sustaining wildlife (Weinstein et al., 2016) by providing invaluable ecosystem services, such as soil formation, nutrient cycling, and habitats for a range of plant and bird species (Foster et al., 2013). Saltmarshes can also act as a physical buffer against climate change impacts, by acting as a natural form of protection against coastal erosion, and absorbing wave and tidal energy before it reaches the shore (Millennium Ecosystem Assessment, 2005). Saltmarshes are highly responsive to environmental changes such as sea level, but in most cases, sediment supply is enough to keep pace with changes in relative sea level (Kirwan et al., 2016). Saltmarshes in the north-west of England have been reported to be laterally accreting, whereas those in the south have seen significant losses due to erosion (Foster et al., 2013). Williams et al (1994) explained that these essential ecological environments have been suffering erosion and decline. Coastal saltmarshes are largely considered to be sinks for organic carbon (Burden et al., 2013, Sousa et al., 2010), as well as trace metals and nutrients (Williams et al., 1994), and are known for their concentration of pollutants. Industrial chemicals such as polychlorinated biphenyls (PCBs) occur widely in the environment and are often found in saltmarsh sediments. Sanger et al (1999) found that tidal creek sediments taken from saltmarshes, particularly in the creek channel, are sources and potential outlets of organic contaminants from the upland environment to deeper estuarine areas. Saltmarsh tidal creeks link the marsh to anthropogenic populations and activities, resulting in higher concentrations of microplastics and other anthropogenic contaminants being found on marshes that occur near densely populated areas (Weinstein et al., 2016).

Due to the lack of research on microplastic pollution in transitional environments such as saltmarshes, our knowledge on the temporal trends for this type of pollution is extremely limited. These environments are highly depositional and have the potential to resolve the temporal evolution of plastic pollution since production began, and improve understanding of their fate in coastal environments. Due to their high rates of sedimentation, saltmarshes can record temporal trends in microplastic accumulation at high resolution. However, their organic rich nature means that extracting microplastic particles from these sediments is extremely problematic. Very few studies have looked at organic rich, fine-grained sediments; therefore, knowledge of suitable methods is limited.

Aims and Objectives

1. To Improve the method for extracting microplastics from organic rich, fine-grained sediment. This will be achieved by;
    - Identifying suitable densities for the extraction specific types and polymers of microplastic particles
2. To investigate temporal trends of microplastic pollution in coastal depositional environments. This will be achieved by;
    - Measuring grain size of dated saltmarsh cores
    - Producing a detailed record of the concentration of microplastic particles from saltmarsh cores
    - Estimating microplastic accumulation rates from dated saltmarsh cores

Literature Review

Sources

Sheavly and Register (2007) explain that due to the high buoyancy of plastics, plastic debris is known to travel along currents for thousands of miles, posing a threat to a number of ecosystems along the way. This makes determining the origins of microplastics problematic. Marine debris can be classified into two main categories, land sources or ocean/waterway sources, and the type and amount of plastic debris is influenced by a number of factors; such as ocean current patterns, proximity to urban/industrial/recreational areas, shipping lanes, and tides (Sheavly and Register, 2007). Browne (2015) states that identifying and eliminating the sources of plastics to the environment is crucial to reducing the social, environmental and economic impacts this type of pollution brings. The two main types of microplastics, primary and secondary, can help to pinpoint specific sources of microplastic pollution.

Primary microplastics

Primary microplastics are manufactured to be of microscopic size, and are most commonly found in cosmetics, such as facial exfoliates and toothpastes. The use of exfoliating cleansers containing plastics has risen dramatically since the 1980s, replacing traditionally used natural ingredients such as oatmeal and pumice (Fendall and Sewell, 2009). In the 1990s, it was found that a minor source of microplastic pollution was derived from liquid hand-cleansers that would have been rarely used by the average consumer. However, Fendall and Sewell (2009) explain that the average consumer today is likely to be

using microplastic-containing products on a daily basis, as the majority of facial cleansers now contain polyethylene microplastics, which are not captured by wastewater plants and will enter the oceans.

Secondary microplastics

Secondary microplastics are broken down from larger plastic debris associated with several chemical, biological and physical processes that occur when plastic is exposed in the marine environment (Cole et al., 2011). Whilst out at sea, plastic debris is exposed to a high amount of photodegradation from sunlight, biodegradation from marine organisms and hydrolysis from the water itself (Andrady, 2011). These processes are ongoing and will continue until larger plastic debris becomes of microscopic size and may continue further to create nanoparticles. On land, secondary microplastics may occur as a result of abrasion of plastic debris at soil surfaces from UV light, or inside the soil profile (Rillig, 2012).

Terrestrial sources

Land based sources are responsible for 70–80% of plastic in the marine environment (Martins and Sobral., 2011, Bowmer and Kershaw., 2010). These sources can be derived from various areas, most commonly urban areas where human population is high. These areas include parks, streets, and residential zones, where littering is common. Wastewater from homes can carry large quantities of thread from clothing, and 'microbeads' from cosmetic waste (Napper and Thompson., 2016). Industrial regions also provide a large quantity of debris due to manufacturing sites (e.g. food, textiles, and technology). Other sources may include litter from anglers and beachgoers (Sheavly and Register., 2007). The type of plastic litter produced from domestic sources mainly include food packaging, clothing thread, drinks containers and cosmetics. Cleaning products, both industrial and domestic, use microplastics as an abrasive scrubber to clean the surfaces of building and machinery (Browne., 2015; Gregory., 1996). This can then enter the marine/coastal environment through sewage and storm water. These pathways can also carry microplastics used in medicine, as ingestible and inhalable methods to deliver drugs to the organs of humans and farm animals can sometimes contain microplastics. However, very little information exists on the type of polymers used for this, as well as their size (Browne., 2015). Water and wastewater treatment plants (WTP/WWTPs) are a common source of microplastics into the environment (Murphy et al., 2016). Microplastic fibres and pellets enter the domestic wastewater infrastructure, but due to their microscopic size, are not always captured or filtered out on site (Fendall and Sewell., 2009; Browne et al., 2011). Previous research has shown that WWTP effluent is a source of plastic fibres, pellets and particles to marine sediment (Browne et al., 2011), coastal waters (Talvitie et al., 2015), riverine sediment (Castañeda et al., 2014), and river surface waters (McCormick et al., 2014). In the UK, around 250% more microplastic waste was found at coastal WWTP than other reference sites, with a higher number present in densely populated areas that received sewage (Browne et al., 2011).

Recently, tyres have been recognised as a significant contributor of microplastic pollution into the environment. In a study by Kole et al (2017), global average emissions are estimated at 0.81 kg /year, with emissions from car tyres being the highest contributor. It was estimated that the relative contribution of tyre wear and tear to the number of plastics ending up in our oceans globally, was in the range of 5 – 10 % (Kole et al., 2017). Horton et al (2017) identified road marking paints as a source of microplastic particles to river sediments. Vogelsang et al (2019) discuss suspected sources of these road dust-associated microplastic particles (RAMP). The report suggests rubber compounds in tyres are the main contributors, followed by polymers used for strengthening bitumen used for road pavements and thermoplastic elastomers for road markings. The majority of these plastics are entering the environment through runoff from roads and road verges during rainfall events.

Marine sources

Out at sea, a number of activities can lead to the dumping of plastic debris. These mostly involve ships, whether it is recreational boats and cruises, or commercial fishing vessels and research boats. Debris can enter the sea through accidental loss, or through poor waste management or illegal dumping (Sheavly and Register., 2007). Fishing gear such as trawl nets and ropes are often discarded and can cause huge problems in the marine environment. Larger plastic litter originates from maritime activities such as fishing, shipping, recreation and offshore industries such as oil and gas. These larger plastics create microplastics through fragmentation, by a number of processes including photolysis, thermal-oxidation, hydrolysis and physical abrasion (Browne, 2015). The terms fragmentation and degradation are often used interchangeably; however, degradation of plastic debris involves reducing the molecular mass of the plastic rather than it simply breaking into smaller pieces (Andrady, 2011). Cole et al (2011) explains that in the past, marine vessels have been a major contributor to marine litter, and it is estimated that during the 1970s the global commercial fishing fleet discarded over 23,000 tons of plastic packaging materials. In 1988, an international agreement was employed banning marine vessels from dumping plastic waste at sea. However, the lack of education and enforcement has resulted in shipping remaining a leading source of plastic pollution in the marine environment (Derraik, 2002). This contributed an estimated 6.5 million tons of plastic to the oceans in the early 1990s (Derraik, 2002). Cole et al (2011) explain that oceanographic models indicate that once in the ocean, plastic debris can accumulate in large gyres. Their fate here is not fully understood, but it is hypothesised that once in the gyres, plastic particles will be exposed to biofouling causing them to fragment until they are small enough to be ingested by marine biota.

Spatial and Temporal trends

To assess the behaviour of plastic particles, their shape, size and density must be considered, as these define the amount of energy needed for their transport (Browne et al., 2010). As well as this, assessing

the hydrodynamic factors and geographical conditions is imperative, as these determine the transport dynamics and accumulation zones of microplastics (Rocha-Santos and Duarte, 2015). Antunes et al (2018), sampled anthropogenic litter from 11 beaches along the Portuguese coast over 2 years, and found that 99% of items were plastic, and 65% of these were microplastics. Higher concentrations of microplastics were found during winter/autumn, near industrial areas and beaches that were exposed to dominant winds. It was determined that the origin of plastic litter was primarily land based (Antunes et al., 2018). Vianello et al (2013) studied the abundance and distribution of microplastics (<1mm) in sediments taken from 10 sites in the coastal area of the Mediterranean region, influenced by both natural conditions and anthropogenic influences. Microplastics were found in all samples, with higher concentrations being observed in landward sites. It was discovered that the spatial distribution of microplastic particles was significantly correlated with the metal pollution index, a synthetic index used to compare the total content of sediment trace metals on the whole (Usero et al., 1996), which suggests possible links with other man-made pollutants and highlights common contamination sources. The study concluded that the abundance of microplastics tend to accrue in low-dynamic areas, showing similar behaviours to other pollutants linked to finer sediments. However, factors such as weathering and biofouling can affect a particles size, shape and density, thus affecting the sinking rates of particles and determining their deposition. This means particles that would normally be found in surface waters, can also be found in marine sediments (Kaiser et al., 2017). Jahnke et al (2017) discuss the impacts of weathering microplastics in the marine environment, and state that biofouling has been found to increase the effective density of floating microplastics, allowing plastics with a lower density than seawater to sink and deposit on the seabed.

Matsuguma et al (2017) studied temporal trends of microplastics (<5mm) in sediment cores taken from Asia and Africa. A range of plastic polymers were found, including Polyethylene (PE), Polypropylene (PP), Polystyrene (PS) and Polyacrylates (PAK). In a canal in Tokyo Bay, larger numbers of particles were found in sediment cores compared to that of surface water samples, suggesting that marine sediments are a significant sink for microplastic particles. The number of particles in the sediment cores increased from the deeper samples to the surface layer of the sediment, and profiles of microplastic concentrations through the cores were consistent with the history of plastic production, suggesting a global increase in microplastic pollution over time. In a study by Turner et al (2019), a radionuclide-dated (^{210}Pb and ^{137}Cs) sediment core was taken from a lake in North London, to assess the temporal record of microplastic pollution in the urban environment. An increase in microplastic accumulation was seen from the 1950s to the present, with relatively low numbers of particles seen before this point. The study suggests that downcore changes in microplastic accumulation, and the colour and types of plastics found, may reflect changes in microplastics

production and usage over time. Zalasiewicz et al (2016) suggests that the presence of microplastics in sediment may result in microplastics being effective stratigraphic markers for Anthropocene strata. Plastics can be found in sedimentary components in both terrestrial and marine environments; however, their presence and distribution on land has been less researched compared to out at sea (Zalasiewicz et al., 2016, Rillig, 2012). Zalasiewicz et al (2016) explain that the use of plastics in agriculture has grown since the 1960s, in practices such as irrigation, poly-tunnels and greenhouse construction, and may now be incorporated within the soil matrix.

Microplastics in Coastal ecosystems

Recent research seems to be moving from plastic pollution out at sea, to the effects of microplastics on coastal ecosystems. These are areas of extremely high importance, and with around 40% of the global population living within 100km of the coast (Small and Nicholls, 2003), studies in these environments are vital. In the UK, over 11 km^3 of water is discharged from water treatment plants, into coastal waters and the ocean (Browne et al., 2011). It is important when looking at microplastic litter in coastal environments to investigate the potential uptake of microplastic particles by marine biota. Li et al (2018) studied the presence of microplastics in wild mussels taken from 8 sites around UK coastal waters. Microplastics were detected in all samples from all sites. It is clear that microplastic pollution is affecting almost all ecosystems, therefore researching a wide range of environments, from marine to terrestrial, is necessary to quantify these affects at a global scale. Martin et al (2019) assessed the role of mangroves as sinks for marine litter by surveying transects in 20 mangrove forests along the Red Sea and the Arabian Gulf, and found that plastic bottles, bags and oil containers dominated the ecosystems. The study suggests the main sources of plastic litter are maritime traffic along both coasts, and currents bringing in ocean-based plastic debris. It is concluded that mangroves do act as sinks for marine plastic litter, as well as barriers for anthropogenic debris before they are dispersed into the marine environment. In Martellini et al (2018) study on microplastic pollution in the coastal areas of the Mediterranean Sea, lagoons and estuaries were found to have the highest levels of contamination.

Microplastics in saltmarshes

Saltmarshes are areas within the intertidal zone that are constantly evolving and are developed by fine sediment transported by water being trapped and stabilised by vegetation (Boorman et al., 1998, Rahman and Plater, 2014). Due to their high rates of sedimentation (Marker, 1967), these environments can show temporal trends at high resolution, and are ideal for geochronological analysis and for reconstructing sea level (Edwards and Horton, 2000; Rahman and Plater, 2014). From this, we can examine a number of environmental events such as storm surges, sea-level change and plant successional change, as well as the accumulation of microplastic pollution since manufacturing began

(Zalesiewicz et al., 2016). At present, very little research exists on microplastic pollution in saltmarshes. Hidalgo-Ruz et al (2012) explain that environments such as saltmarshes with low hydrodynamic energy are likely to act as retention systems for microplastic particles, and because of this it is important that plastic fragmentation, transfer and accumulation in these environments is investigated. Viehman et al (2011) characterised marine debris on saltmarshes around North Carolina and found that all sites contained debris and the majority of this was composed of plastic. Therefore, the presence of microplastics in these ecosystems is almost certain, as larger plastic debris will be exposed to a number of processes on the marsh such as photo-oxidation and hydrolysis, which will cause them to break down further to microscopic size (Andrady, 2011).

Very little is known about the properties that influence the fragmentation, distribution and deposition of microplastics in estuarine ecosystems (Lima et al., 2014). The distribution of particles, both natural and man-made, is determined by their shape, size and density, which ultimately define the amount of energy needed for their transport (Browne et al., 2010). Various factors can be attributed to the deposition of microplastic debris, such as vegetation concentration and surface gradient, which vary spatially across saltmarshes (Thornton and Jackson, 1998). Vegetation density strongly influences the flow dynamics across saltmarshes (Christiansen et al., 2000), as well as its ability to retain marine debris. Vegetation on saltmarshes is often characterised by halophytic plants in lower marsh areas, with reeds and other less salt tolerant plants higher up on the marsh. *Spartina* often colonises the outer area of saltmarshes, and is known to effectively trap silt (Marker, 1967), suggesting it may also be effective at trapping plastic particles of a similar size. The particle size distribution of saltmarsh sediments ranges from sandy soils through to silts and clays, displaying a high geological variability (Williams et al., 1994).

In a study by Weinstein et al (2016) into the degradation of plastics in a saltmarsh habitat, it was concluded that the rate of degradation occurs fairly quickly in these types of habitats. Three types of high-density plastics; polyethylene, polypropylene and polystyrene, were deposited into a saltmarsh habitat. 150 plastic strips, 50 of each polymer type, were attached to wooden boards and buried in a shallow trench in an intertidal saltmarsh. The marsh was inundated with water at high tide for approximately 6hrs a day and were exposed during low tide for approximately 6hrs a day. Plastic strips were removed (10 of each polymer) at 4 weeks, 8 weeks, 16 weeks and finally 32 weeks. The study suggests that microplastics are most likely produced as a result of the delamination on the surface of larger plastic debris. Evidence of this can be seen in the SEM images of the plastics after being deposited in the saltmarsh for 8 weeks, which show various marks of surface erosion such as cracks, pits and broken edges. What is less certain is the environmental fate of these plastics once they are released from the surface of the larger plastic debris.

Study Site

The North West coastline is comprised of extensive areas of saltmarsh, sand flats and mud flats. Along the south region of the coast are population centres with major industrial developments, such as Liverpool, Southport and Blackpool, making this stretch of coastline one of the most built up in Great Britain. The north of the region however, is much more rural and much of the land is used for agriculture (Barne et al., 1996).

Fig. 2: Map showing the Morecambe Bay area and Walney Island, with a map of the UK in the inset (Digimap).

Morecambe Bay (Fig. 2) is a macrotidal estuary with the largest area of intertidal mud and sand anywhere in the UK (34,339 ha) (Mason et al., 1999). In recent years, the area of saltmarsh in the region has increased, as the pioneer saltmarsh plant S*partina alterniflora* has expanded rapidly over the tidal flats. However, vegetation in some areas of Morecambe Bay and the Duddon estuary has reduced significantly due to heavy grazing and turf cutting. Tidal currents in the area can be classified as low, at approximately 2 m/sec. The tidal range for the region is high, with a spring tidal range exceeding 8 m. Tidal surges, produced by rapidly moving atmospheric depressions increasing the flow of water into the Irish Sea from the Atlantic, may influence tidal ranges in the area. During a storm in 1990, wave heights of over 4.5 m were recorded during high water. These storm events may also impact water flow through the Irish sea, which generally flows northwards and is relatively weak (Barne et al., 1996).

Walney Island is a sand and shingle island sandwiched between Morecambe Bay and the Duddon estuary, forming a barrier against the Irish Sea to the west. It is one of England's largest Islands, with nature reserves protecting important flora and fauna. This includes a large number of lesser black-backed and herring gulls, as well as a range of other bird species (Brown, 1967). Both the north and south of the island are experiencing coastal erosion, as well as natural defences on the island such as cliffs, and although extensive protection measurements are in place, restricting erosion of the backshore, this poses the risk of increasing erosion of the lower foreshore by stopping the supply of eroded sediment from elsewhere (Barne et al., 1996).

Biggar marsh is a large wetland area located on the sheltered eastern coast of the Island. The site was chosen because of the existing geochemical data recorded for the marsh from Rahman et al (2013), which compared peak ^{137}Cs activity in sediments to peak radionuclide discharge from Sellafield. Low-level radioactive waste can be seen in the marsh as a result of the deposition of fine grains when the tidal flow velocity is significantly reduced at the turn of the tide, combined with the clumping of fine grains due to the mixing of freshwater and seawater within the estuary (Rahman and Plater, 2014).

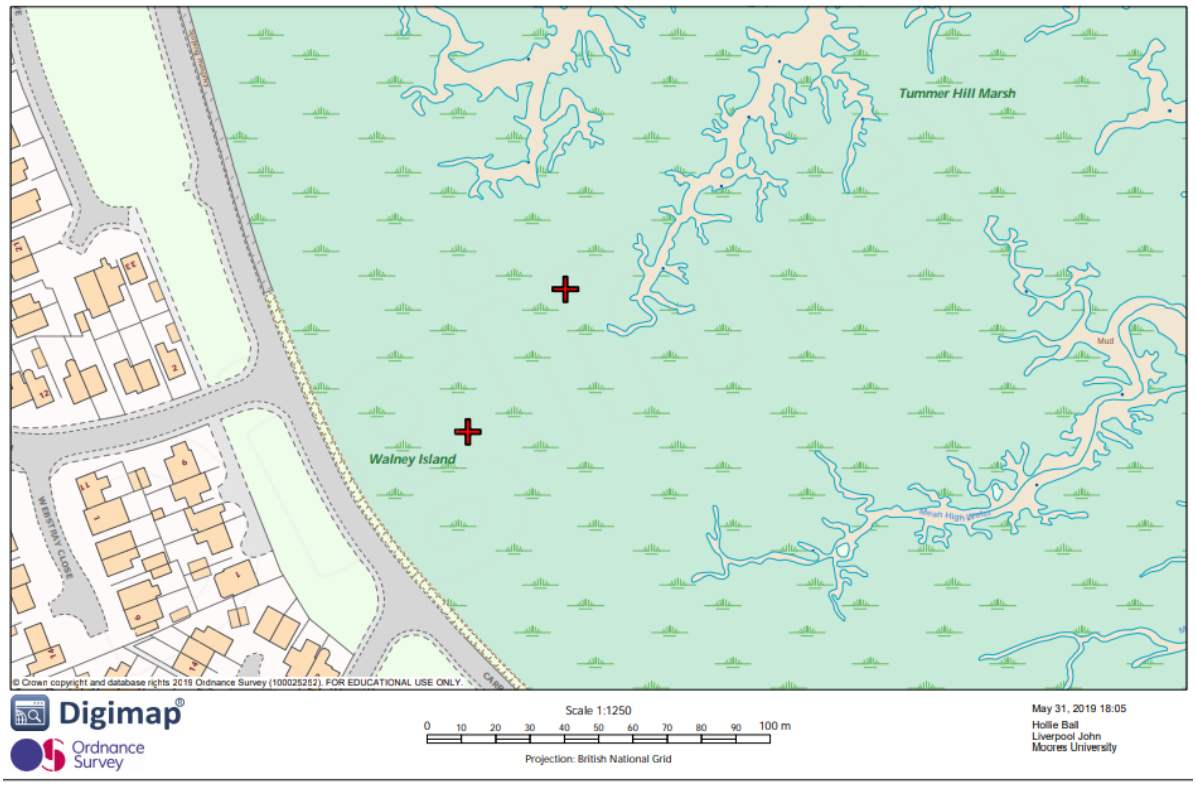

Fig. 3. Location of both cores taken from Biggar marsh, Walney Island. Core 1 located in the upper middle marsh, and core 2 located in the lower middle marsh near a creek system (C1 = SD18200 67283, ~36.6 m from roadside, C2 = SD18232 67324, ~48.9 m from C1).

In a study by Baugh (2019), the morphology of Biggar marsh is discussed. According to the study, the marsh is comprised of three main zones, each dominated by different species of vegetation. Zone 1 (0 – 12 m), the high marsh, has a sharp decline in elevation (0.33 m) over just 12 m. The vegetation in this zone is comprised mainly of *Phragmites australis*, a species that is found nowhere else on the marsh. Zone 2 (12 – 80 m), known as the middle marsh, shows further elevation falls of 0.46 m. The vegetation in this zone is comprised mainly of *Limonium*, *Triglochin maritima*, *Puccinellia sp*., *Carex salina*. In zone 3 (80 – 210 m), the lower marsh, tidal creeks are introduced. Species such as *Halimilone portulacoides, Armeira maritima, Spartina alterniflora, Plantago maritima*, colonise this area.

Walney Island and the surrounding coastline is vulnerable to plastic pollution on beaches and intertidal environments, from both land and marine sources. Anthropogenic litter can reach the coast via river discharges, land run-off, urban waterways and sewage outfall. As well as this, the concentration of human population and industrial areas along the coast increases the likelihood of a build-up of plastic debris. Marine sources, such as fishing and recreational activities, are also a viable source of plastic litter. The channels around Walney and Barrow are important routes for commercial vessels and cruise ships, which may also contribute to marine pollution. Due to a lack of freshwater input, the Walney channel is more of a tidal inlet rather than an estuary, with the south of the channel separated from the north during low water. The channel receives discharges from sewage, some of which contain low concentrations of toxic metals from trade effluent (Vivian, 1985). There are a number of industrial sites across the bay on Barrow Island, and many of these businesses are located around the Buccleuch Dock, which runs into the Walney Channel. These include a towing and salvage yard, a concrete plant and energy companies, all of which have the potential to be sources of marine litter. Biggar marsh runs parallel to residential area, and across the bay from South Walney is the Lancaster wastewater treatment works. The United Utilities Poaka Beck wastewater and sewage treatment works and Acorn Industrial services are located just off the estuary on North Walney, which are all potential sources of microplastic pollution.

Review of Current Methods

Microplastic research has developed rapidly over the last decade, with more and more studies looking into the effects microplastics are having in the marine environment and beyond. However, due to this rapid development, there is a lack of uniformity in the methodology used for sampling and quantifying microplastics (Hidalgo-Ruz et al., 2012). Most of these variations are to do with extraction techniques, sampling practices and size limits (Cauwenberghe et al., 2015). In most literature, microplastics are referred to as being either ≤1mm (Claessens et al., 2011), or ≤5mm (Law and Thompson, 2014), with the latter being the most reported in the literature to date (Horton et al., 2017), however there is no universal agreement on size definition for microplastics. Lower size limits are often defined by the type of equipment used, for example when investigating the presence of microplastics in marine studies, plankton nets with mesh sizes of ~0.33 mm are used meaning any particles smaller will not be captured (Law and Thompson, 2014). Some studies define lower size limits as small as 1µm (Käppler et al., 2016, Horton et al., 2017), however the detection of particles this size is almost impossible. Hidalgo-Ruz (2012) found that most studies reported values above 500 µm for sediment samples, and above 300 µm for seawater samples. Andrady (2011) has suggested adding the term "mesoplastics" to differentiate between small plastics visible to the human eye and those only discernible with use of microscopy. The methods explained below are just a few examples of the different techniques used for microplastic extraction. To be able to ascertain a true representation of microplastic pollution around the world, results need to be generated from validated methods that are consistent in the field of microplastic research (Quinn et al., 2017). However, these methods must be adaptable to suit the type of substrate, for example, extracting plastics from organic rich mud samples will be more complicated than extracting particles from sand samples with very little to no organic matter.

Extraction

Sieving / filtering

For both sediment and water samples, this step can vastly reduce the amount of time spent on removing larger materials and allows for specific lower size limits to be determined. In a study by Hidalgo-Ruz et al (2012) on methods used for microplastic identification and extraction, it is noted that studies using sediment samples used either one sieve, or cascades of two or three sieves. Van Cauwenberghe et al (2013) wet sieved sediment samples, first through a 1 mm mesh sieve and subsequently on a 35 µm mesh sieve. Studies focusing on sea surface samples used either 1, 5 or 6 sieves, with mesh sizes ranging from 0.038 to 4.75 mm, and all studies included a mesh size of 1mm (Hidalgo-Ruz et al., 2012). However, this again creates an issue for comparing data, as mesh sizes vary significantly across studies. For example, Correia Prata et al (2019) explain that defining a standardised pore or mesh size will allow comparison between research, but this can become problematic when

work is dependent on protocol constrains, therefore creating a universal sampling protocol is vital (Correia Prata et al., 2019).

Sample Purification

Loder and Gerdts (2015) explain that the purification of microplastic samples is essential, especially when using instrumental analyses such as FTIR or Raman spectroscopy for the purpose of identifying specific polymers. This step aims to remove any organic or inorganic materials in the sample that could affect the correct identification of plastic particles. For most water samples, the use of a purification step is not always necessary, but if some purification is required, a digestion step using HCl (Typically 10 %), H_2O_2 (Typically 30 %) or enzymes should be enough to remove most of the undesirable biological material (Correia Prata et al., 2019, Karlsson et al., 2017). However, samples such as wastewater and those taken from coastal systems are likely to be rich in organic material, and a standard purification step will not sufficiently remove these organics. Cooper and Corcoran (2010) washed samples in a Branson ultrasonic cleaner with deionised water for 4 minutes to remove any loose debris, NaCl and $CaCO_3$, before drying samples for 45 minutes. Loder and Gerdts (2015) explain that the use of ultrasonic cleaning could potentially break down aged and brittle plastic debris resulting in secondary microplastics, therefore this method should be carefully considered. Liebezeit and Dubaish (2012) treated dried beach sediment samples with H_2O_2 (30 %) to remove any natural organic material, after a preliminary experiment suggested this treatment did not affect the plastic particles. However, in a study by Nuelle et al., (2014) it was found that although 30% H_2O_2 was an ideal chemical for removing around half of the organic matter, a number of noticeable changes in some polymers were observed, and a chemical reaction between the chemical and the polymers was indicated through the development of gas bubbles. Cole et al (2014) also state that although H_2O_2 is an effective agent for removing organic matter from sediment samples, the use of 35% H_2O_2 over a relatively long exposure period of 7 days will only remove around 25% of OM present, and the remaining material is bleached. This may cause issues when it comes to identifying polymer types and origins.

Tagg et al (2017) suggest that for organic rich samples, the use of Fenton's Reagent (a mixture of H_2O_2 and ferrous ion, Fe^{2+}) can rapidly and effectively reduce the number of organic compounds in a sample through oxidation. The study concludes that Fenton's reagent offers a simple, high speed and low-cost method for processing microplastics present within environmental samples (Tagg et al., 2017). However, this method may have an effect on some polymers, which could be problematic when it comes to identification. Cole et al., (2014) have developed a method for the digestion of biological material that does not have an adverse effect on microplastics. This technique is described as a rapid method in which biota-rich seawater samples and marine organisms are treated with a proteolytic

enzyme to digest biological material without damaging any of the microplastics present within the sample. The method is capable of digesting >97% of biological material found in sub-surface marine samples, making the isolation of microplastics much easier. However, this method is less cost-effective than the use of certain chemicals and is a much lengthier process.

Density Separation

In studies where microplastics were separated from sediment samples, 65 % used the density separation technique (Quinn et al., 2017). Most previously published studies depend on density separation using salt solutions such as sodium iodide (NaI), sodium chloride (NaCl), and sodium polytungstate ($Na_6(H_2W_{12}O_{40})\ H_2O$) (SPT). Plastics have a range of densities dependent on the polymer type, with most common consumer plastics having densities ranging from 0.8 to 1.4 g cm-3, therefore denser salt solutions, the main ones being SPT and NaI, are preferred (Quinn et al., 2017). However, these are often considered too expensive for bulk samples (Tagg et al., 2015). Alternative techniques have been suggested, such as elutriation and flotation (Claessens et al., 2013, Nuelle et al., 2014), and have proven effective in separating microplastics from marine sediments. However, these techniques are not suited for samples with high concentrations of organic matter, such as wastewater or saltmarsh samples, as these will most likely contain natural particles showing similar densities to those of microplastics. For these, an alternative approach is necessary to isolate the microplastics from the organic rich sediment, and the removal of organic matter in the purification step is preferred.

Quinn et al (2017) tested the efficiency and validity of various brine solutions, including sodium chloride (NaCl), sodium bromide (NaBr), sodium iodide (NaI), and zinc bromide ($ZnBr_2$). The study found a general trend of increasing microplastic recovery with increasing solution density, with NaI and $ZnBr_2$ having significantly higher rates of microplastic recovery. However, although NaI showed similar recovery rates to $ZnBr_2$ and is known to be cheaper and more environmentally friendly, it turned filter papers black, which made isolating and identifying the microplastics almost impossible. The study concluded that $ZnBr_2$ is the most effective brine solution for the extraction of microplastics, and by reusing the solution through careful filtration and clean-up methods, the cost and hazardous effect on the environment can be significantly reduced.

Corcoran et al (2009) used sodium polytungstate, a non-toxic heavy liquid (Madella et al., 1998), to separate microplastic particles from beach sediment taken from strandlines at eighteen beaches on the island of Kauai. To help determine plastic types, each sample was placed in SPT at a density of 1.4 g /mL where particles with a density <1.4 floated to the surface and were filtered into beakers. These particles were then mixed with SPT at a density of 1.2 g /mL, followed by ethanol/water mixtures of various densities. SPT has previously been mentioned as a viable solution for the extraction of microplastics from sediment, and although it is expensive, it can be reused if filtered and cleaned

correctly. However, there is currently no data on microplastic recovery rates for SPT (Quinn et al., 2017).

Coppock et al (2017) created a portable method to separate microplastics from different types of sediments, from fine silt/clay to coarse sand, using density floatation. The Sediment-Microplastic Isolation (SMI) unit uses zinc chloride at a density of 1.5 cm^{-3} to extract microplastics from sediments in a single step, with a mean efficiency of 95.8%. The method is described as cheap, reproducible and easily portable, so the SMI can be used in both the lab and the field, although the toxicity of zinc oxide reduces its utility. Crichton et al (2017) have created a novel method involving the use of an Oil Extraction Protocol (OEP) to extract the microplastics from sediment samples. The method takes advantage of the oleophilic properties of plastic polymers, with the hope that when mixed with sediment containing microplastics, the polymers will become trapped in the oil layer, which is then filtered out. The novel method offers a cost-effective, less hazardous alternative to the more commonly used density separation techniques.

Mitigating Contamination

During sample collection and preparation, it is likely that samples will be exposed to plastic contamination; from particles in the air and unclean lab equipment, to fibres falling from polyester clothing. These contaminants can lead to a significant overestimation of microplastic pollution. Contamination is almost impossible to eradicate completely, but there are several protocols used by researchers to mitigate microplastic contamination throughout their studies. Cole et al (2014) suggest using Milli-Q to rinse all apparatus before use, and in some cases, apparatus was acid-washed. Ensuring sample preparation is conducted in a sterile environment is vital, and samples and equipment should be covered wherever possible to minimise exposure to airborne particles. Wearing protective equipment and clothing that contains only small/if any amounts of plastic fibres would be ideal, and the use of clean, 100% cotton lab coats is preferred (Quinn et al., 2017). One of the most important procedures to use when attempting to monitor contamination are ‘blanks’. These must be clean samples containing no microplastics. The blank samples are put through the same method as all other samples, and any plastics found once analysed will be taken into consideration when looking at the total microplastic concentration from all other samples (Cole et al., 2014).

Identification

Visual Sorting

Once microplastics have been separated from the initial sample, they are filtered for microscopic analysis. Most studies rely on visually sorting samples to identify any plastic particles for further analysis, however this method allows for the misidentification of plastics for other extracted organic and inorganic material of a similar size (Hidalgo-Ruz et al., 2012, Shim et al., 2016). Some studies chose

to identify microplastics under a microscope using specific criteria, to standardise microplastic selection and avoid misidentification of microplastics. These criteria specify that microplastics should have no cellular or organic structures visible, fibres should be equally thick throughout their entire length and should not taper at the end, coloured particles are homogenously coloured, fibres are not segmented or twisted, and particles are not shiny (Norén., 2007, Song et al., 2015).

Spectroscopic Analysis

Correctly identifying particles as plastic is crucial when attempting to quantify concentrations of microplastics pollution, as a large percentage of particles that visually resemble microplastics are not confirmed as such when analysed with spectroscopic techniques (Hidalgo-Ruz et al., 2012). Cotton fibres and other natural fibres are often mistaken for microplastics, and this could vastly overestimate the abundance of microplastics in samples (Song et al., 2015). Spectroscopic techniques can be used to provide a more reliable identification of the plastic particles. These approaches include pyrolysis gas chromatography paired with mass spectrometry (pyrolysis GC/MS), Raman spectroscopy, and more commonly Fourier-transform infrared (FT-IR) spectroscopy (Löder and Gerdts, 2015). Spectroscopic analysis has identified individual fragments of common plastics as small as 20 µm in diameter (Law and Thompson, 2014). FTIR analysis can be used to identify plastics on filters, and once the sample has been extracted, digested and filtered, does not require any pre-sorting (Käppler et al., 2016). However, if using chemicals such as 30 % H_2O_2 during digestion, this may have noticeable effects on some polymers (Nuelle et al., 2014). FTIR imaging does have the disadvantage of limited diffraction, therefore smaller particles (<10µm) cannot be detected. Käppler et al (2016) also found that microplastics <20µm were significantly underestimated when using this method. However, the study found that Raman imaging was able to detect microplastics as small as 5 µm, although measurement times for this method are much longer if a high-quality spectra is required. Both techniques vary in the amount and size of microplastics detectable, and can vary in polymer identification, as Käppler et al (2016) explain that Raman imaging can detect PVC particles easier, whereas FTIR imaging seems more sensitive to polyesters.

Method developed for this study

After reviewing the literature about current microplastic analyses, a novel method using multiple density separations was developed to extract microplastics from organic rich, fine grain sediments from a UK saltmarsh, minimising chemical treatment. A series of density separations were used in the assumption that this will reduce the amount of organic material in each sample, extract a wide range of polymer types without chemical alteration, and give some idea as to the polymer type based on which density it was extracted in. The density range started at 1.8 – 1.6 g cm^{-3} in the hope that this

would remove most of the heavier organic material. Sodium Polytungstate ($Na_6(H_2W_{12}O_{40})\ H_2O$) (SPT) was chosen as the best solution to use, due to the fact it is a heavy, non-toxic liquid (Madella et al., 1998) and can be reused if filtered and cleaned correctly making it cost effective and environmentally friendly. A size fraction of <1 mm was chosen for this study.

All equipment was washed three times before and in-between uses using Milli-Q water. 100% cotton lab coats were worn at all times to prevent any transfers of synthetic clothing to samples. Some equipment used (centrifuge tubes, Normesh *MiniSIV*) did contain plastic; however blank samples were run and results were taken into account. All equipment was covered with foil when not in use.

Microplastic Analysis

Sampling

Two cores (1 m) were extracted from Biggar Saltmarsh on Walney Island (Fig. 3), Cumbria, in September 2016, at the approximate altitude of the MHWS (~8.15 m) (Rahman et al., 2013). The first core was taken from the upper/transitional area of the marsh (SD 18200 67283), ~ 30 m from the roadside where vegetation was well established. The second core was taken approximately 50 m further into the marsh (SD 18232 67324), where tidal inundation is more frequent, and creeks are present. Cores were extracted with a 10 cm diameter metal gouge corer and placed in a plastic half-pipe covered in foil to prevent contamination and were then wrapped in foil before being wrapped in cling film to ensure they were airtight and stored under refrigeration. In the lab, ~4 cc of sediment was taken from each core, every 1 cm. These subsamples were placed into 250ml glass beakers, and 10 ml of 0.5% Sodium Hexametaphosphate (Calgon) was added and left overnight to disaggregate the clay minerals (Bartoli et al., 1991). All beakers were covered with a clean watch glass to prevent airborne contamination.

Microfiltration

Each sub sample was wet-sieved, first through a 1 mm sieve to remove larger particles and organic matter. Particles that were < 1 mm were collected in a 1 L beaker, which was then filtered through a Normesh *MiniSIV* (6 µm) using a fast, fine stream of water. Once the water running out of the filter was clear, the contents on top of the filter were transferred back into 250 ml beakers using Milli-Q water. This was repeated for every subsample with the filter sheets being washed thoroughly between samples to prevent cross contamination and changed every 20 samples. These samples were left to settle for 24hrs, and when a clear separation could be seen, the water was removed using a 10 ml pipette.

Pre-treatment

All samples were then treated with 25 ml of 10% Hydrochloric acid (HCl) to remove Calcium Carbonate ($CaCO_3$). After 24 hours the samples were placed on a hot plate (40°C) in a fume cupboard for 60 minutes until the reaction had stopped and left for a further 24 hours to settle. The HCl was then syphoned off and the samples were cleaned with 25 ml of Milli-Q water twice to remove excess HCl. The samples were washed into 50 ml test tubes and centrifuged for 10 minutes at 2500 rpm. After the sample had settled out, the excess water was syphoned off.

Density Separation

To ensure the highest range of plastics were extracted, whilst using the least amount of harsh chemicals, samples were run through four different density separations using sodium polytungstate (SPT). Densities of 1.8, 1.6, 1.4 and 1.2g cm^{-3} were used to give the best recovery rate for plastics whilst leaving most of the OM in the higher densities. The original density of the (SPT) was 2.8gcm^{-3}. This was diluted down to 1.8 g cm^{-3} by adding Milli-Q water, using a hydrometer to measure the desired density.

40 ml of the solution was added to all subsamples, and each was placed on a vortex for 10 seconds to thoroughly mix the sediment, before being placed into a centrifuge for 10 minutes, at 2500 rpm. After a clear separation could be seen, the solution at the top of the tube containing the floating particles was poured into a 5 cm Hartley pattern three-piece filter funnel with the Normesh filter sheet (6 µm), and placed over a 1 L Buchner flask, with the remaining sediment at the bottom of the tube being discarded. Once the sample was on the filter paper it was transferred, using Milli-Q water, into clean 50 ml tubes. The tubes were placed into the centrifuge for 10 minutes at 2500rpm, and the water was removed from the top using a vacuum aspirator. The samples were then transferred into smaller 15 ml tubes using Milli-Q water, and this was again centrifuged and vacuumed off until only the sediment remained. 14 ml of 1.6 gcm^3 SPT was then added to each sample before being placed into a centrifuge at 2500rpm for 10 minutes. Once a clear separation could be seen, the floating particles (containing particles ≤1.6) were filtered off by pouring the solution into a 25 mm Hartley pattern three-piece filter funnel with GFF filter sheet and transferring the sediment into a different 15 ml tube for the next stage of density separation. The sediment remaining in the previous tube contained particles with a density >1.6gcm^3 and <1.8gcm^3. This sediment was transferred onto a 25mm Whatmann GF/A filter paper (0.7 µm) for microscopic analysis, using a 25mm Hartley pattern three-piece filter funnel. This method was repeated for densities of 1.4 and 1.2 gcm^3. To reduce the risk of contamination, foil was used to cover the opening of the funnel in between uses, and filter papers ready for microscopic analyses were kept in foil cases. Overall, densities included 1.8-1.6gcm^3, 1.6-1.4gcm^3, 1.4-1.2gcm^3 and 1.2gcm^3.

Identification

All subsamples were examined under a microscope (MEIJI EMZ –TR) at 4.5 X magnification. The size and colour, as well as the type of microplastic, were recorded for each subsample. Microplastic types were defined using the table below (Hidaglo-Ruz et al., 2012) and the following criteria from Nor and Obbard (2014) and Norén (2007);

1. Particles that are bright/unnatural and homogenously coloured
2. Particles with no visible cellular or organic structures
3. Fibres are equally thick throughout their length and do no taper at the end
4. Particles are not shiny

TYPE OF MICROPLASTIC	DEFINITION	POSSIBLE SOURCES
FRAGMENT	Hard, rough plastic particle	Bottles/containers
PELLET	rounded, solid plastic particle	Facial cleansers; cosmetics; medicine
FIBRE	Thin, elongated plastic	Fishing line; shopping bags; clothing

Table 1: Definitions and possible sources of microplastic pollution (Hidalgo-Ruz et al., 2012)

Blank Samples

Samples were taken from around 70 cm of each core, where plastic pollution would not be expected. Both sub-samples were processed using the exact same methodology as before. The same equipment was used throughout and was cleaned thoroughly between uses. 100% cotton lab coats were always worn to reduce contamination from clothing. Fibres were found in each separate density for both cores. No other types were found in any of the blank samples. The fibres were counted and categorized by density, and the mean and SD for each density were calculated. The mean fibre count was subsequently removed from each density for every sub-sample.

Density (g cm-^{3})	Mean MPs ± SD
1.8 - 1.6	7 ± 3
1.6 - 1.4	6 ± 1
1.4 - 1.2	4 ± 0.5
1.2	3

Table 2: Mean ± SD number of plastic particles extracted from each density for both cores in blank samples

^{137}Cs Analysis

Work carried out at the Environmental Radioactivity Research Centre (ERRC), University of Liverpool

To investigate the presence of ^{137}Cs on the marsh, a separate core was collected from the same co-ordinates as C1 from Biggar marsh for gamma spectroscopy using a High Purity Geranium detector (Ortec HPGe GWL) shielded with lead and copper. The core was split into 10 cm sections and each section was placed into a foil tray and was broken up using a metal spatula. All samples were dried at 105°C for 24 hours before being placed into the detector. A background check using Europium was ran overnight prior to analysis. 'ProSpect' software was used to analyse the gamma spectroscopy data, with each sample running for one hour.

The age model created for this study is a crude representation of the geochronology of the marsh. It is based on the mean sedimentation rate for Biggar marsh in 2008, which according to Rahman et al's (2013) study was 0.47 cm yr^{-1}, and peak ^{137}Cs outputs from Sellafield. Saltmarsh sedimentation rates are driven by sea level (Foster et al., 2013), and therefore will not remain constant over time. There is very little information on the variability of sediment accretion rates at Biggar marsh. Mason et al (1999) explains that from looking at patterns of erosion and accretion for Morecambe Bay over the last century, it appears the sediment budget for the bay is positive. This however, does not consider the erosional outer coast, where there is a negative budget (Comer and Hansom, 1994). The accuracy of the age model is therefore uncertain and does not fully represent the time elapsed between samples due to likely changes in sedimentation rate.

Particle Size Analysis

To measure the particle size distribution for both cores, sub-samples of *ca.* 2 g of sediment were used every 1 cm down-core. Each sub-sample was placed into a clean 250 ml glass beaker, and 25 ml of concentrated (30 %) H_2O_2 was added to remove any organic matter. All samples were watched cold

until reactions slowed and were subsequently left overnight. Samples were then placed on a hot plate and watched again until reactions had stopped. Once reactions had stopped, all samples were topped up to 150 ml with Milli-Q water and left to settle. The remaining liquid was pipetted off all samples. To avoid grain flocculation, a shallow layer (~ 10 ml) of 0.5 % $NaPO_3$ (Calgon) was added to each sample. All samples were added to a 40°C oven until most of the liquid had evaporated and the sample resembled a paste. For each sample, a small amount of the paste was added to a laser granulometer (Beckman Coulter LS-13320). Results were analysed using GRADISTATv8 (Blott and Pye, 2001).

Statistical Analysis

All microplastic data along with particle size data were analysed using SPSS. A normality test was conducted prior to analysis using the Shapiro-Wilko test, as the sample number was <50. Due to the non-normal nature of the data, the Mann Whitney U test was used to test for differences, and the Spearman's rank test for correlations between variables.

Results

The chapter below considers the results from a series of analyses on cores taken from Biggar marsh, Walney Island, to investigate microplastic pollution on the marsh. Sedimentological parameters are considered first, with core descriptions and particle size analyses for both cores. Following this, results from the methodological development of the study are presented, focusing on the extraction percentages for the different densities used during microplastic extraction. From this, temporal changes for the cores are presented, starting with geochronological dating using ^{137}Cs outputs, followed by the down-core changes in microplastic concentrations and the link this may have with the sedimentology of the marsh.

Sedimentology

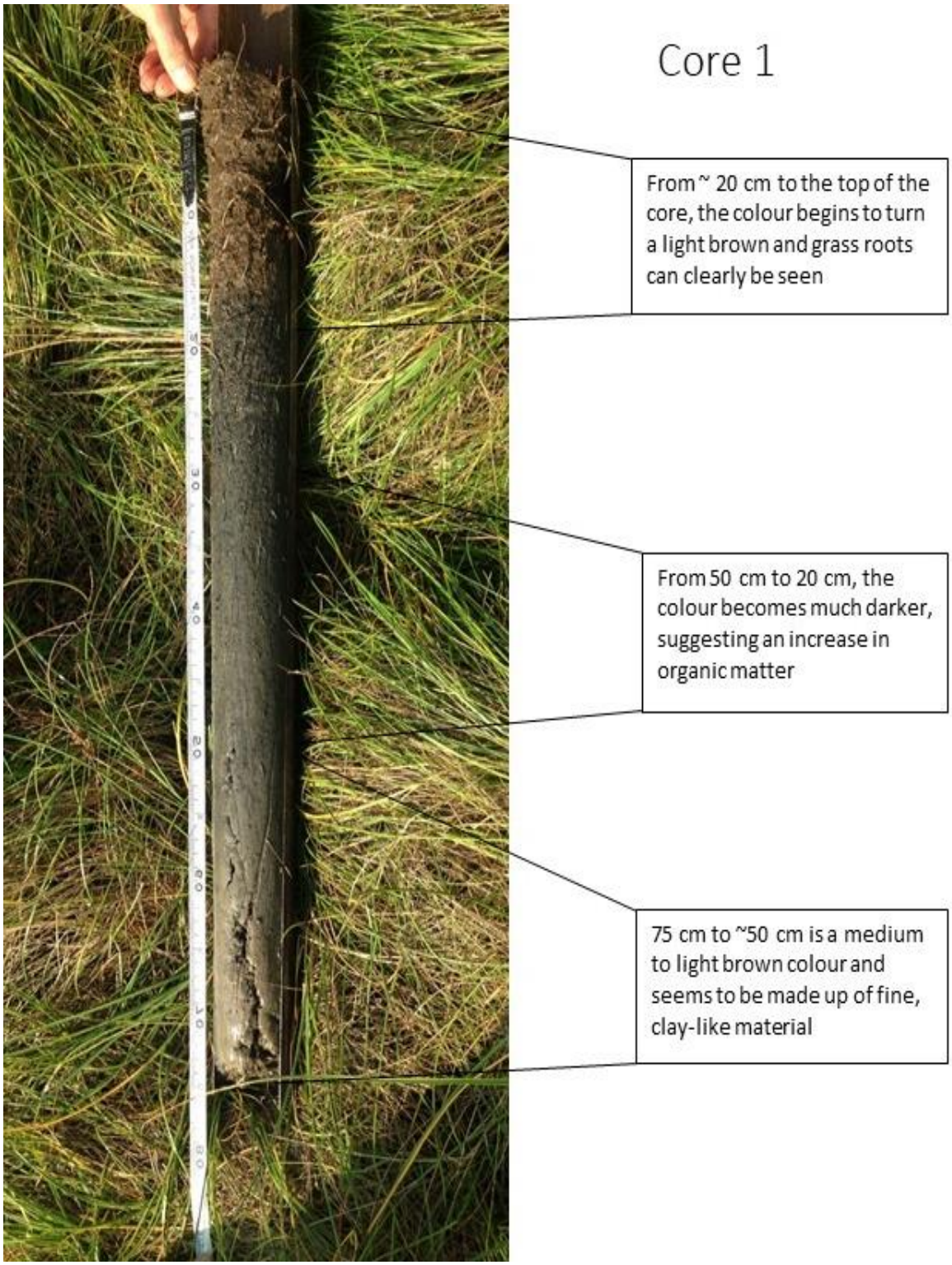

Fig. 4: C1 taken from the upper marsh (SD 18200 67283)

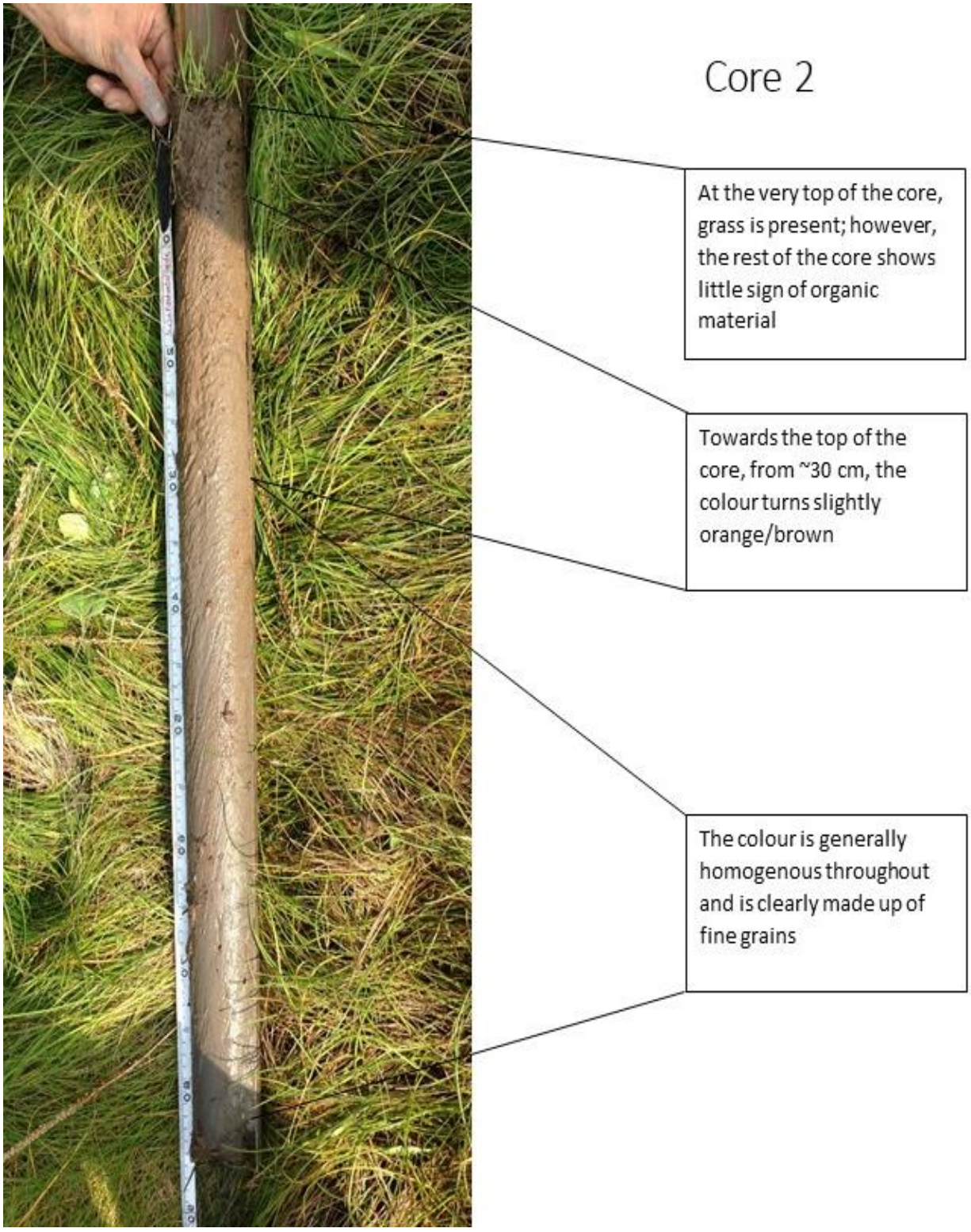

Fig. 5: C2 taken from the middle marsh (SD 18232 67324)

Particle Size Analysis

There is a significant difference between the mean grain size in C1 compared with C2 ($U_{40,40}$ = 417.4, p= 0.000). There are no significant differences between the sorting, skewness and kurtosis in C1 and C2.

C1: From 40 cm – 30 cm, the core is made up of a mixture of coarse to fine silts (3.8 ϕ – 7.5 ϕ), going into very fine silts (7 ϕ) between 30 cm to 25 cm. From 24 cm up to 10 cm is mostly coarse silt (4 ϕ – 5 ϕ), with some subsamples at around 14 cm – 12 cm moving into very fine sands (3.5 ϕ – 3.9 ϕ). The top 10 cm of the core is comprised mainly of fine to very fine silt (7 ϕ – 8 ϕ) with the top subsample shifting to more coarse silts (4.9 ϕ).

The core is poorly to very poorly sort throughout, with a slight shift from 10 – 20 cm to poorly/moderately sort. From 10 – 25 cm the grains shift from fine skewed to very fine skewed, and platykurtic to leptokurtic.

C2: The particle size for core 2 is relatively homogenous throughout, comprising mostly of fine to very fine silts (6.4 ϕ – 8 ϕ). The grains are poorly to very poorly sort, and are fine skewed and platykurtic.

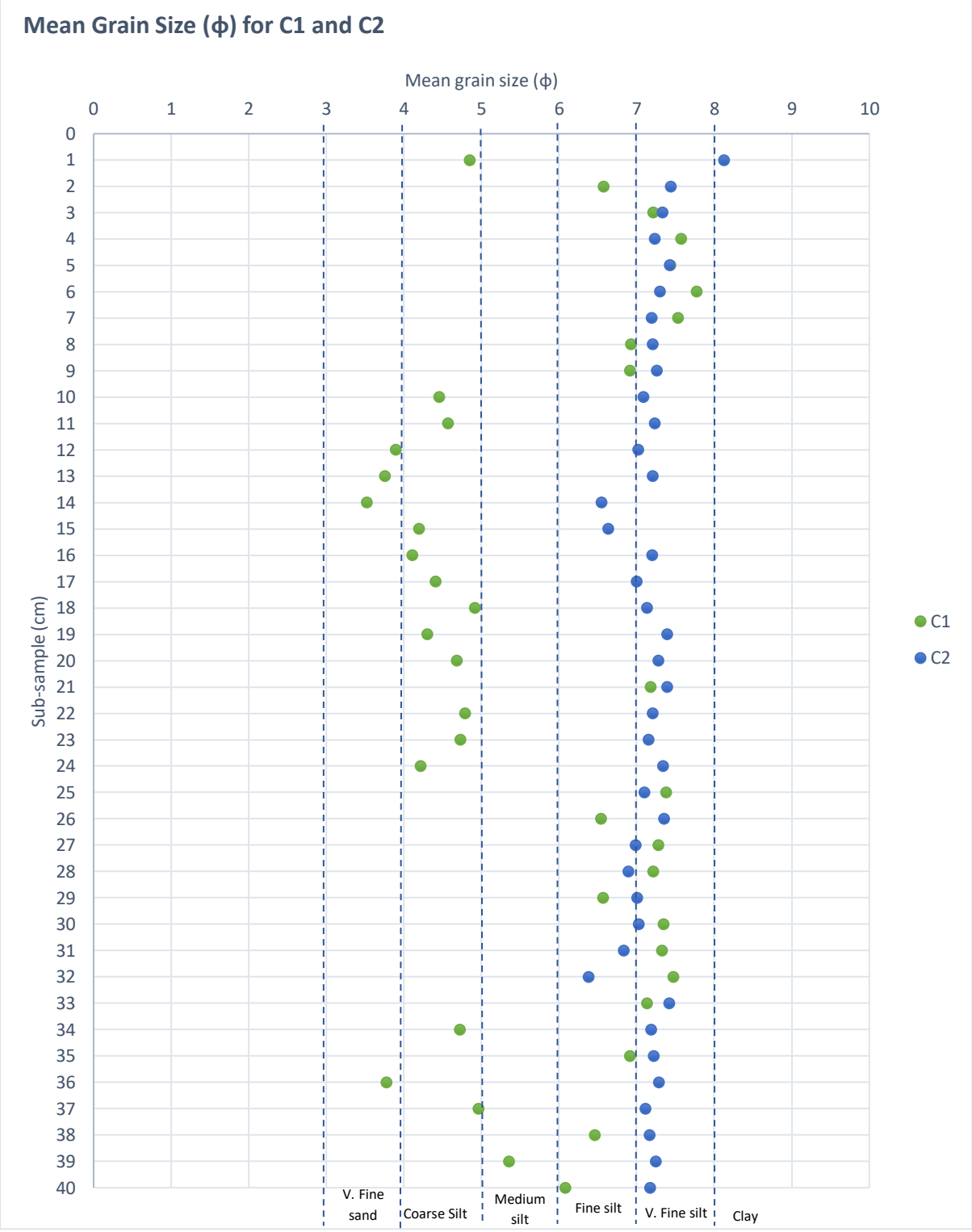

Fig. 6: Down-core profile of mean grain size (ϕ) for both cores

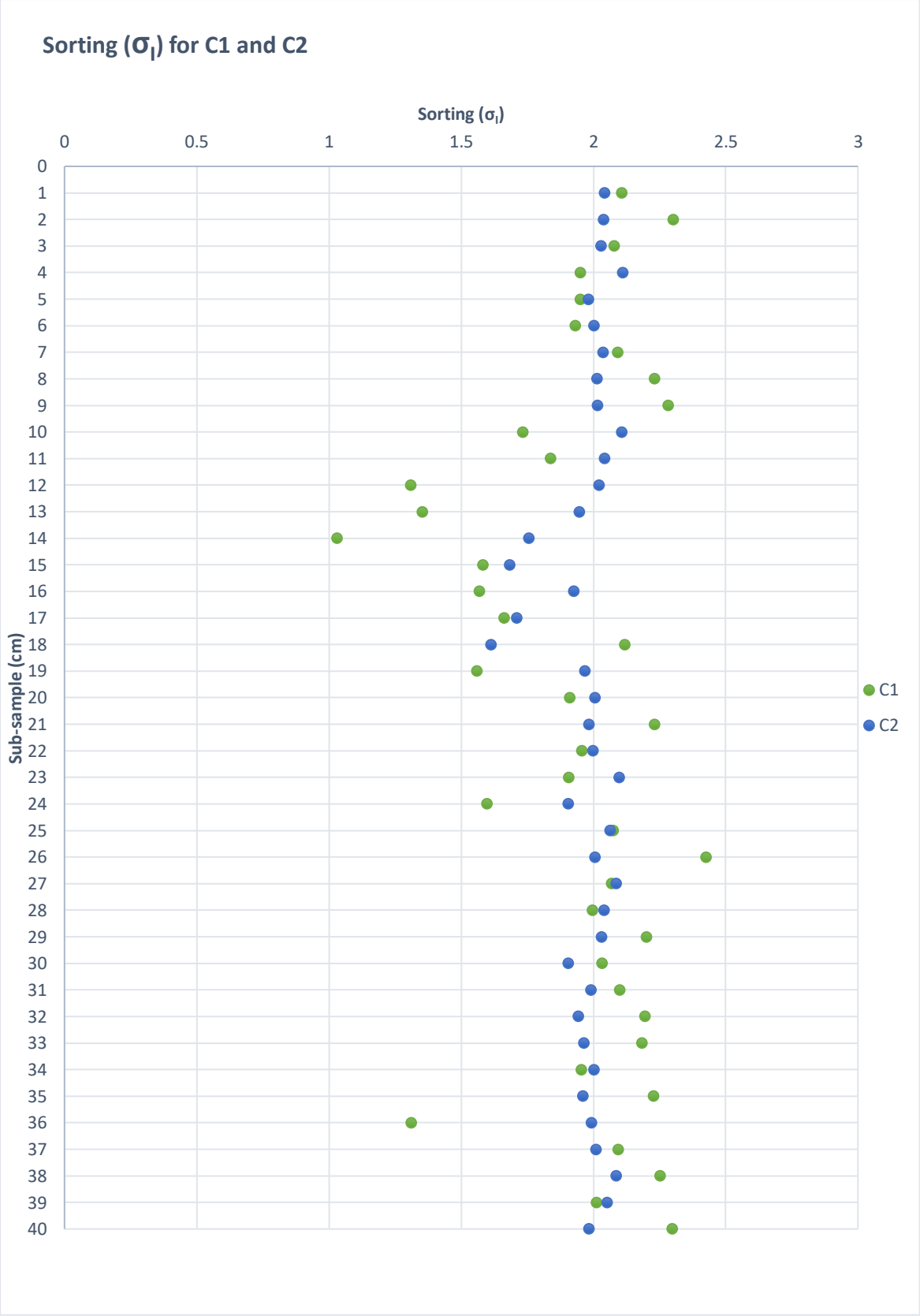

Fig. 7: Down-core profile of grain size sorting (σ_I) for both cores

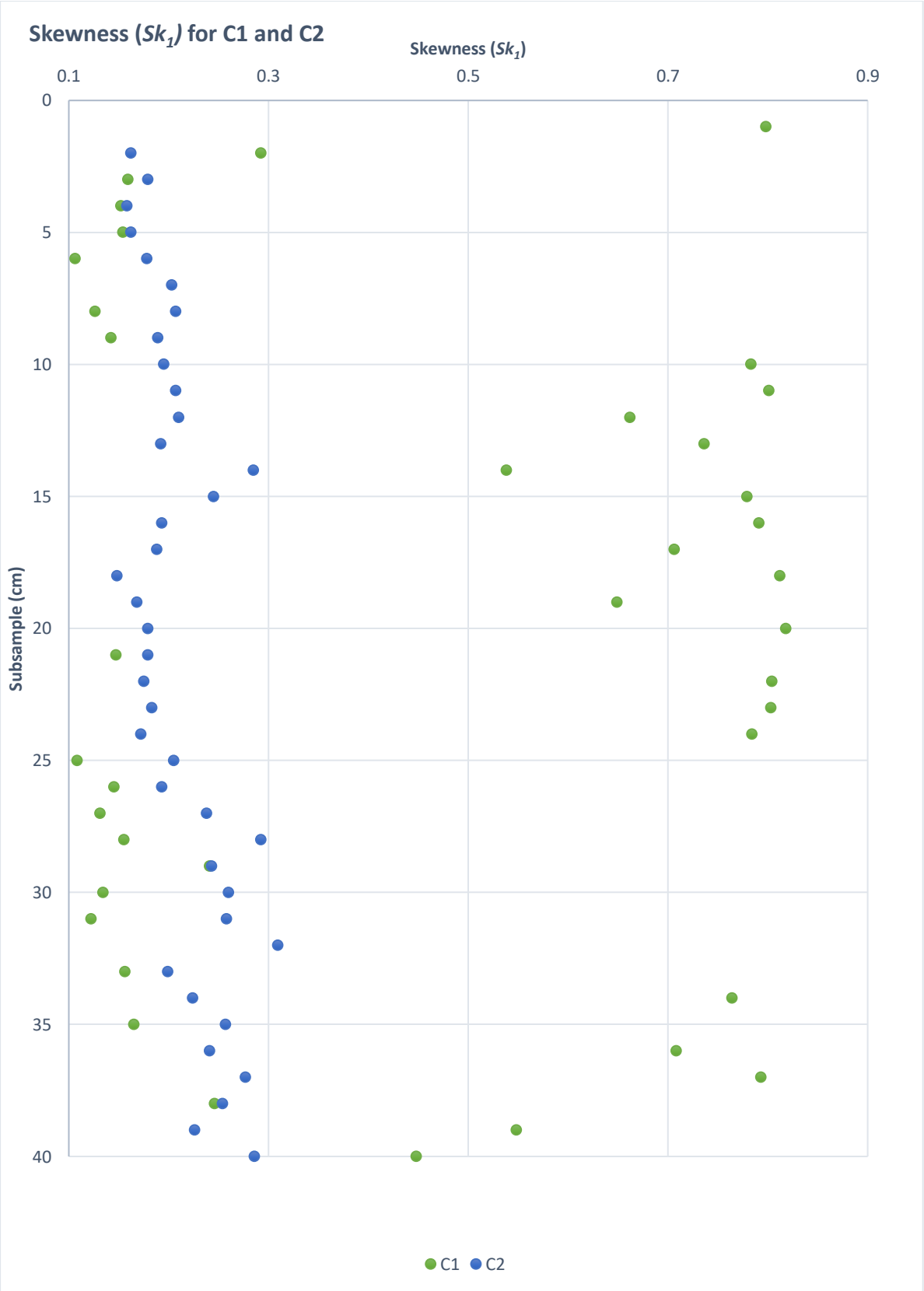

Fig. 8: Down-core profile of grain size skewness (Sk_1) for both cores

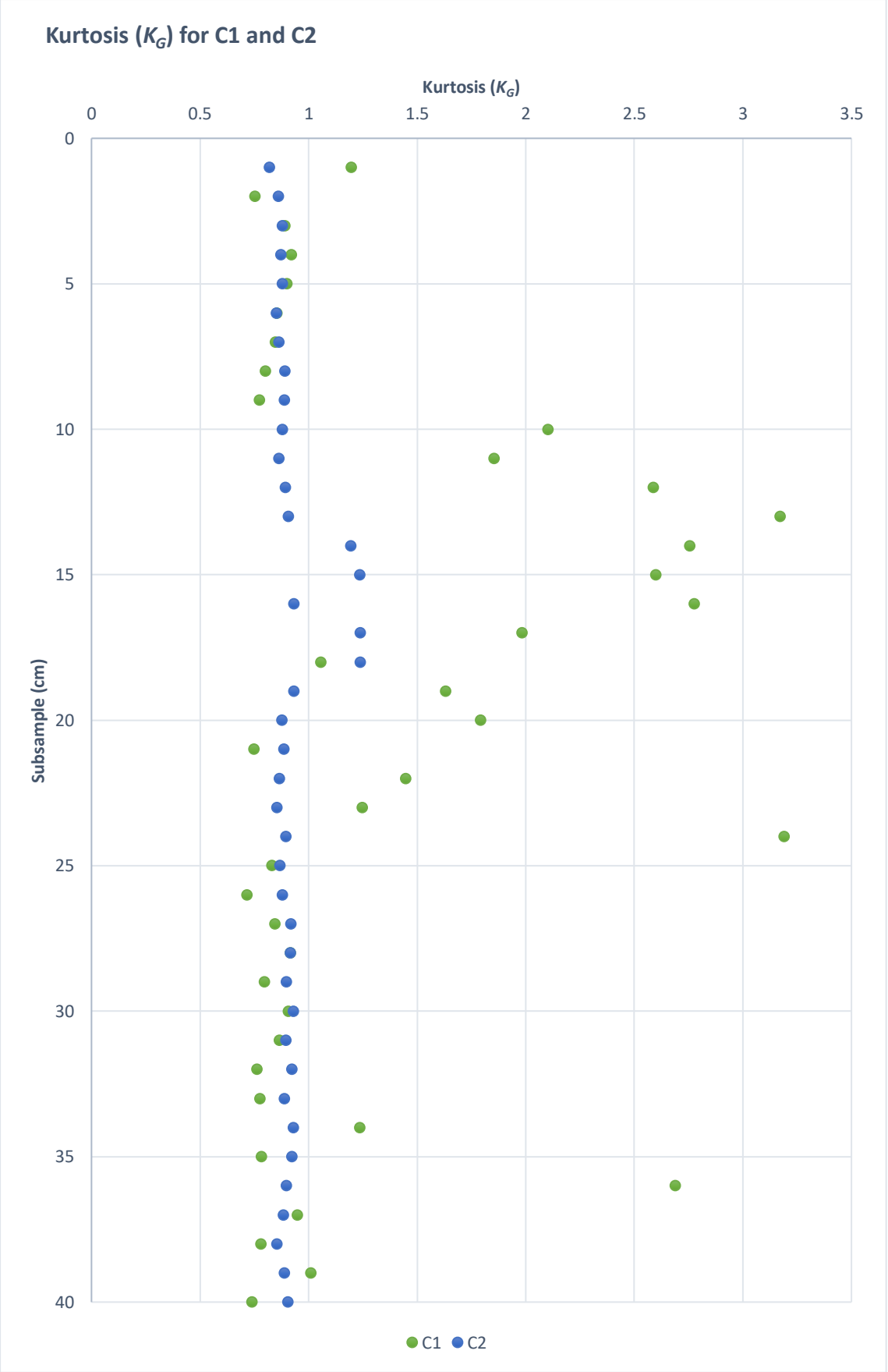

Fig. 9: Down-core profile of grain size kurtosis (K_G) for both cores

Methodological Results

Microplastics were found in almost all sub-samples for both cores taken from Biggar marsh. Pellets were the most common plastic particles found in both cores (80 % ± 3), with much lower proportions of fragments (16 % ± 4) and fibres (4 % ± 0.7) (Fig. 10). There is no significant difference for microplastics found in C1 compared with C2 ($U_{40, 40}$ = 797, p= 0.977).

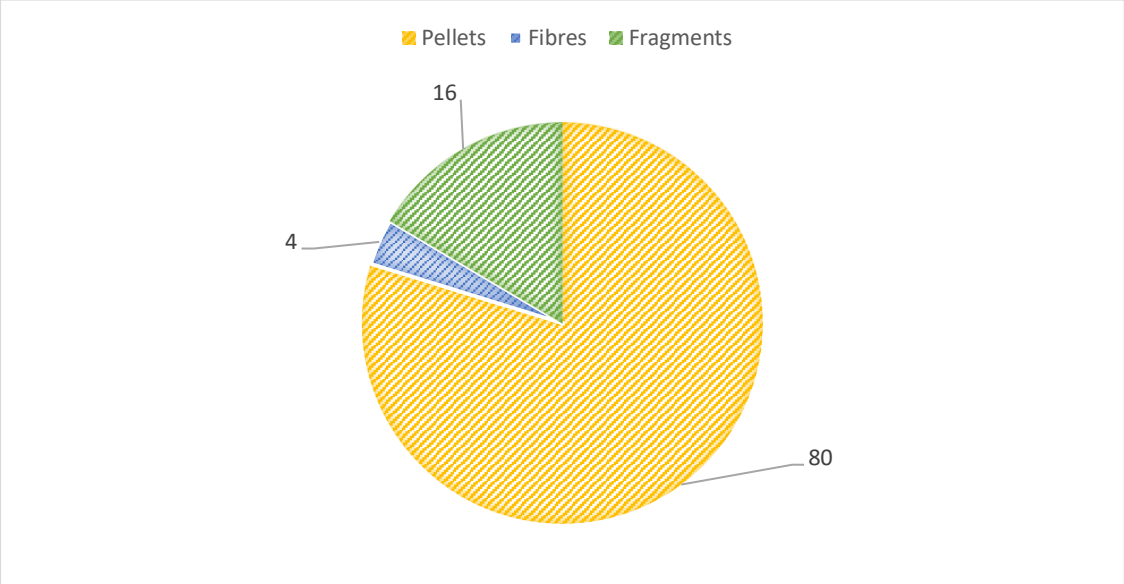

Fig. 10: The proportion (%) of each type of microplastic particle found in both cores.

It was expected that in each density range, certain types of plastic would be extracted based on the polymer density. Table 3 lists the known density ranges of common consumer virgin plastic types (Morét-Ferguson et al., 2010). Table 4 contains the raw data for the number of microplastic particles extracted in each sub-sample for C1, and the density the number was extracted from. Table 5 shows the same data for C2.

Polymer Type	**Density (g cm^{-3})**
Polyethylene (PE)	0.917 – 0.965
Polypropylene (PP)	0.9 – 0.91
Polystyrene (PS)	1.04 – 1.1
Polyamide (nylon) (PA)	1.02 – 1.05
Polyester (PES)	1.24 – 2.3
Acrylic	1.09 – 1.20
Polyoximethylene (POM)	1.41 – 1.61
Polyvinyl alcohol (PVA)	1.19 – 1.31
Polyvinylchloride (PVC)	1.16 – 1.58
Polyethylene terephthalate (PET)	1.37 – 1.45
Polymethylacrylate (PMMA)	1.17 – 1.20
Alkyd	1.24 – 2.10
Polyurethane (PU)	1.2

Table 3: List of known density ranges for different plastic types (Hidalgo-Ruz et al., 2012).

C1	1.8 - 1.6			1.6 - 1.4			1.4 - 1.2			1.2			Total		
	Pel	Fib	Frag	Pel	Fib	Frag	Pel	Fib	Frag	Pel	Fib	Frag	Pel	Fib	Frag
1	2	1	1			2					2	1	2	3	4
2	3						1		2	1	2		5	2	2
3			2	4			1			1		1	6		3
4									5						5
5	4		1	7		4	4		4	1			16		9
6				3		1	7		3		1		10	1	4
7				1		1	4				1		5	1	1
8				4	3	1	3					1	7	3	2
9					1	2			2					1	4
10			1	2			3		1				5		2
11						1	2		1				2		2
12							4		1			1	4		2
13															
14															
15															
16				1		3	1		3			1	2		7
17				2								1	2		1
18				3			1			1			5		
19	4			4		2	4						12		2
20	3			4			5						12		
21	1			8		1	4						13		1
22	1			15			5						21		
23				13									13		
24				13			4		1				17		1
25				14			6						20		
26	3			16		1	13		2			1	32		4
27				11		1	2						13		1
28	2			5		1	2		1				9		2
29	2		1	3		1							5		2
30															
31															
32															
33															
34															
35	2			3			3		1				8		1
36				6			3			1			10		
37															
38				3									3		
39	1												1		
40				3					2				3		2
Total	28	1	6	148	4	22	82	0	29	5	6	7	263	11	64

Table 4: Raw data for the number of particles extracted from each density range for C1

C2	1.8 - 1.6			1.6 - 1.4			1.4 - 1.2			1.2			Total		
	Pel	Fib	Frag	Pel	Fib	Frag	Pel	Fib	Frag	Pel	Fib	Frag	Pel	Fib	Frag
1															
2				1			1						2		
3				1									1		
4	1			2		1	5		1		1		8	1	2
5	1						4						5		
6	1									1			2		
7	1						5				2		6	2	
8			1				5						5		1
9				1		1	2			3	1		6	1	1
10			1	3		3	5		1				8		5
11	1		1	2			4		2				7		3
12	2			1			5			1			9		
13				2		2	2						4		2
14						1	2						2		1
15				1			2	1					3	1	
16				3			5						8		
17	2			1			2		3				5		3
18	2			7			3		2				12		2
19	2			5			5				1		12	1	
20	4			3		3	4						11		3
21	2			6			3				1		11	1	
22	1			10		1	5						16		1
23				7			8		1				15		1
24	1			4		2	4			1			10		2
25				7			3						10		
26	2			8		1	6	2	2		2		16	4	3
27				12			7		1				19		1
28				3		1	3		1			1	6		3
29			1	6			3						9		1
30				1		1	1		1	1			3		2
31				2			3		1				5		1
32	1			4			2		1				7		1
33			1												1
34							2						2		
35															
36							2		1				2		1
37				1			1						2		
38															
39											2			2	
40	1								1				1		1
Total	25	0	5	104	0	17	114	3	19	7	10	1	250	13	42

Table 5: Raw data for the number of particles extracted from each density range for C2

For both cores, the highest percentage of plastics were recovered between 1.6 – 1.4g cm^{-3} (46 %), with 39 % extracted between 1.4 – 1.2 g cm^{-3}(Fig. 11). The majority of pellets (Fig. 12) from both cores were recovered from the density range 1.6 – 1.4 g cm^{-3} (49 %), with 38 % coming out at 1.4 – 1.2 g cm^{-3}. A very low percentage (2 %) of pellets were extracted at 1.2 g cm^{-3}. Almost all fibres (67 %) for both cores were extracted at a density of 1.2 g cm^{-3} (Fig. 13). Fragments (Fig. 14) were mainly extracted between 1.4 – 1.2 g cm^{-3} (45 %) and 1.6 – 1.4 g cm^{-3} (37 %).

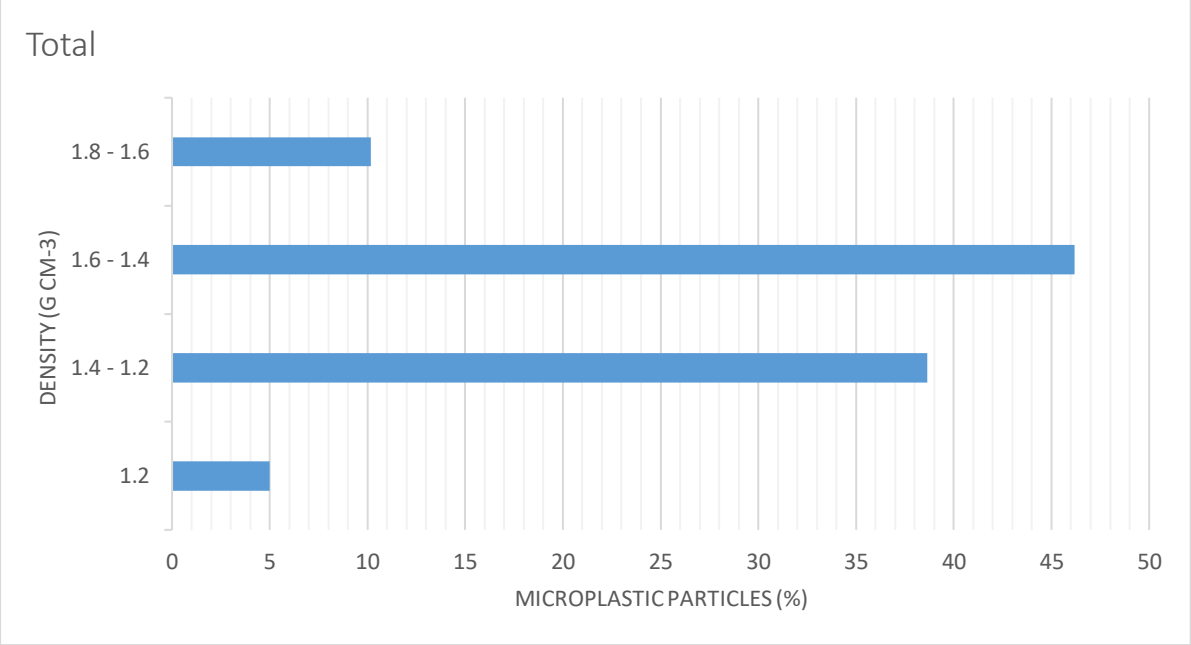

Fig. 11: The total proportion (%) of all microplastic types extracted from each density range for both cores

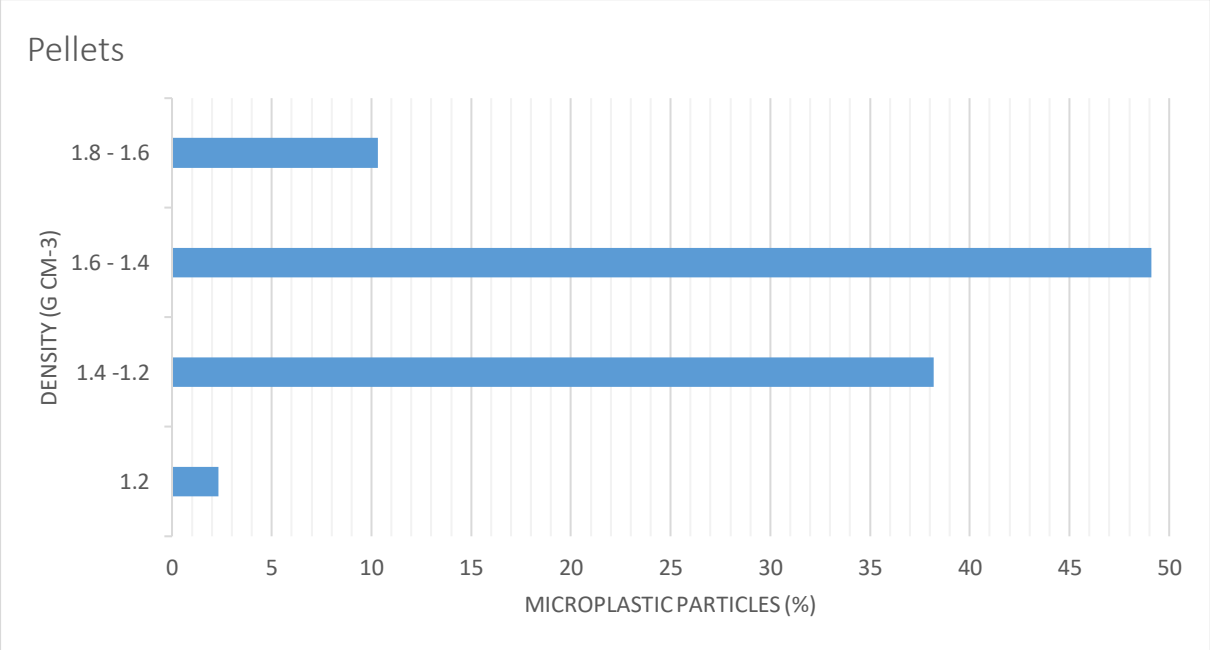

Fig. 12: The total proportion (%) of pellets extracted from each density range for both cores

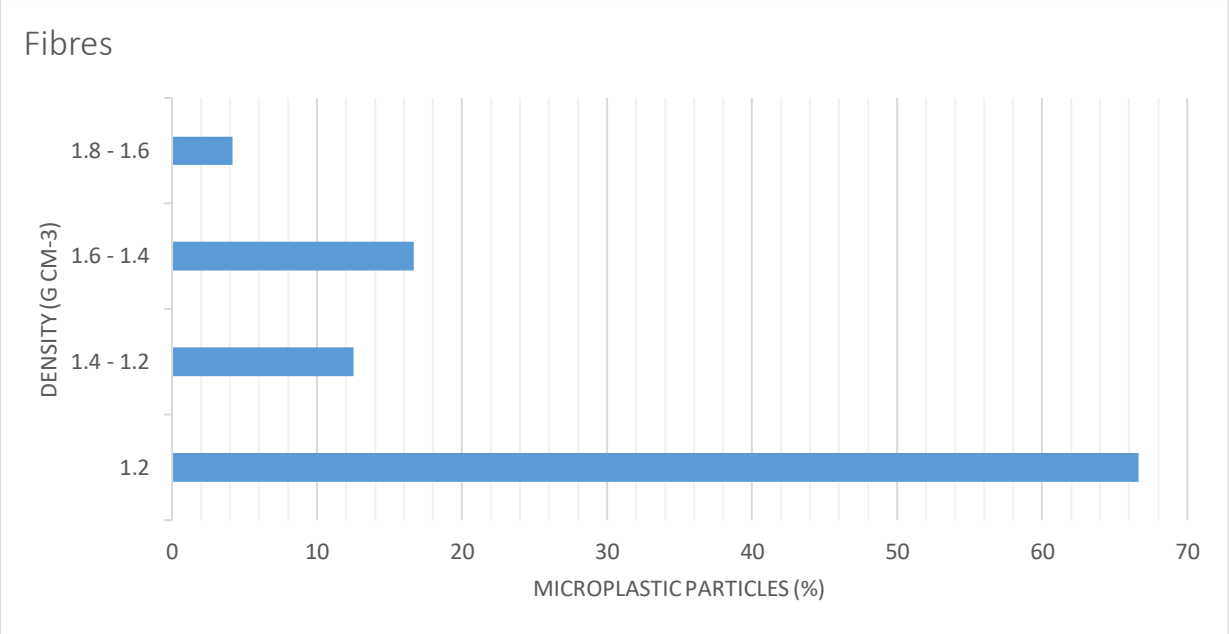

Fig. 13: The total proportion (%) of fibres extracted from each density range for both cores

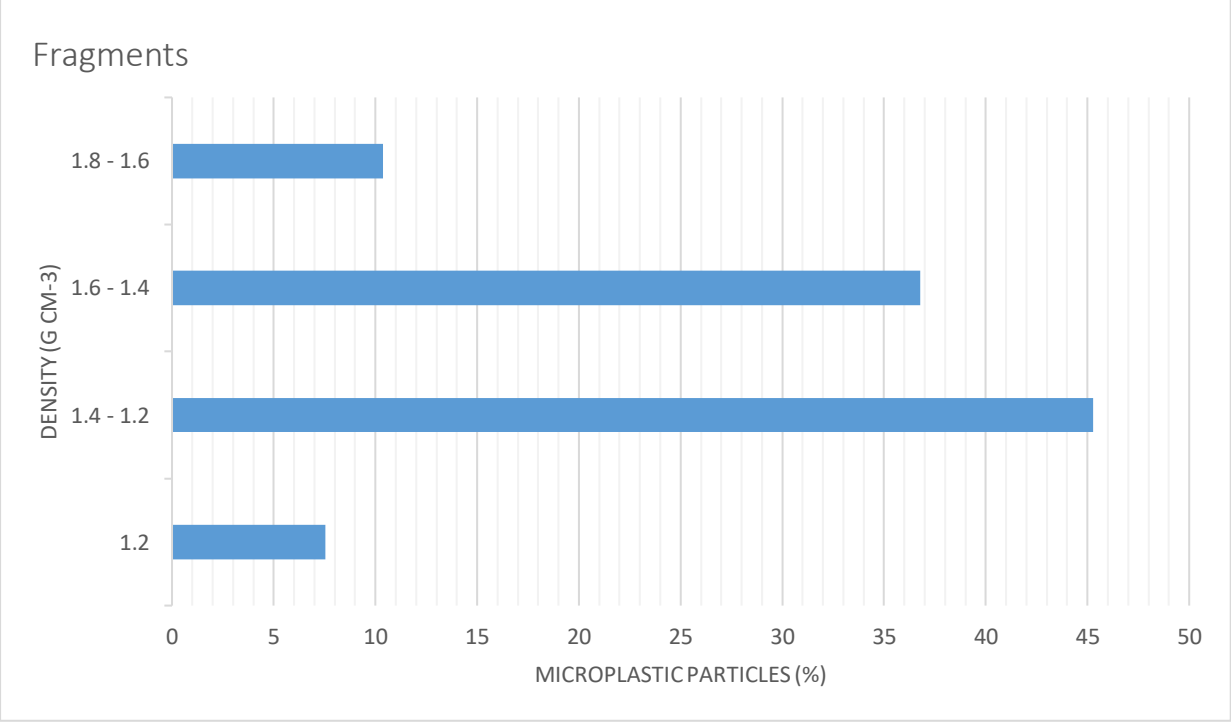

Fig. 14: The total proportion (%) of fragments extracted from each density range for both cores

Temporal Changes

Geochronology

The ^{137}Cs data taken for this study peaks at the latter end of the 10 - 20 cm section (Fig. 15). According to Rahman et al (2013), peak activities in cores taken from the same marsh represent increased discharge from Sellafield between the years 1974-1978, with ^{137}Cs peaking in 1975, around 13 – 15 cm down-core. The study calculated a mean sedimentation rate of 0.47 cm $^{-1}$yr for Biggar marsh. The cores for this study were taken in 2016, and since 2008 when samples were collected by Rahman et al (2013), the marsh should have accreted by ~4 cm according to the mean sedimentation rate. This puts the peak ^{137}Cs levels at around 17 – 19 cm, which matches the ^{137}Cs peaks found in this study. From this data, a down-core profile of estimated dates was generated (Fig. 16).

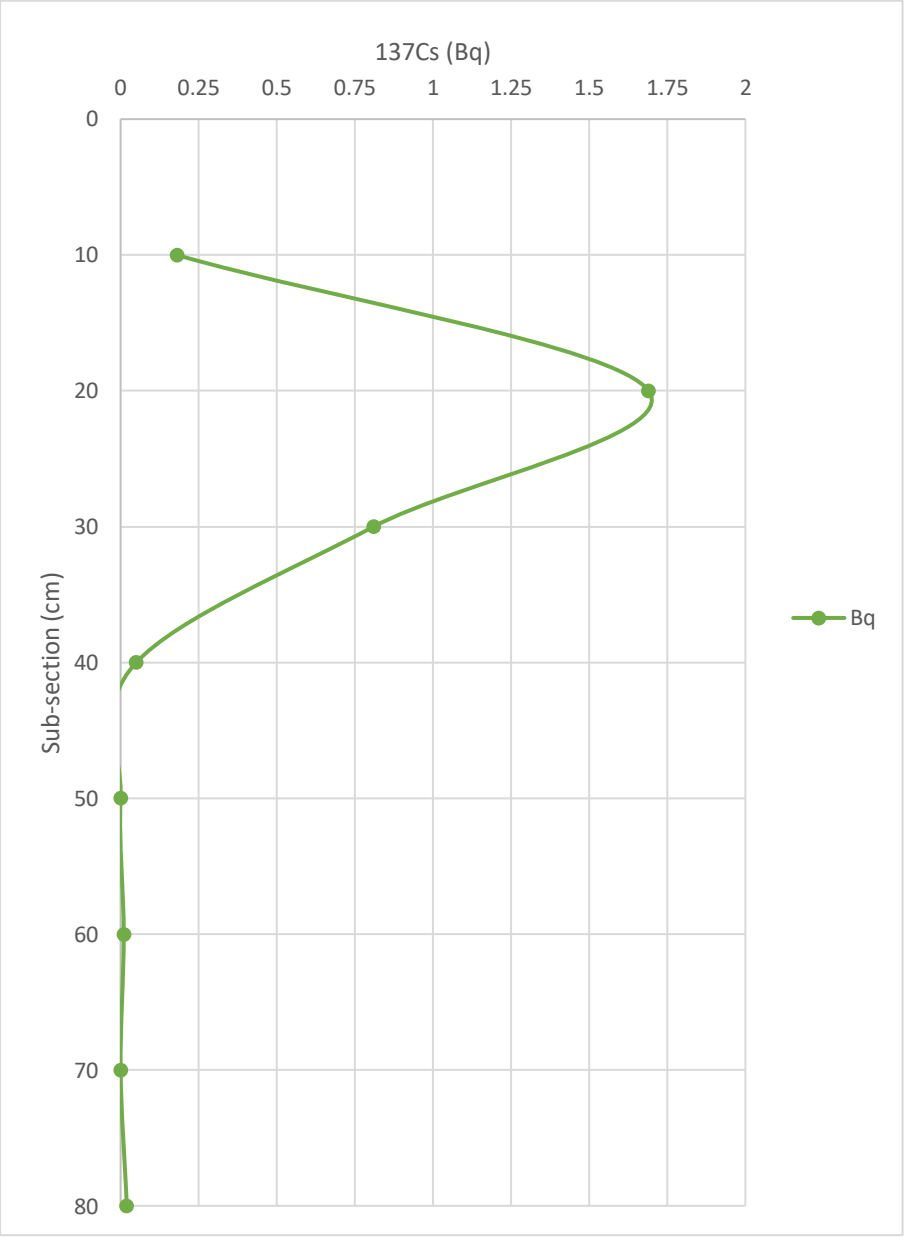

Fig. 15: Down-core profile of ^{137}Cs data

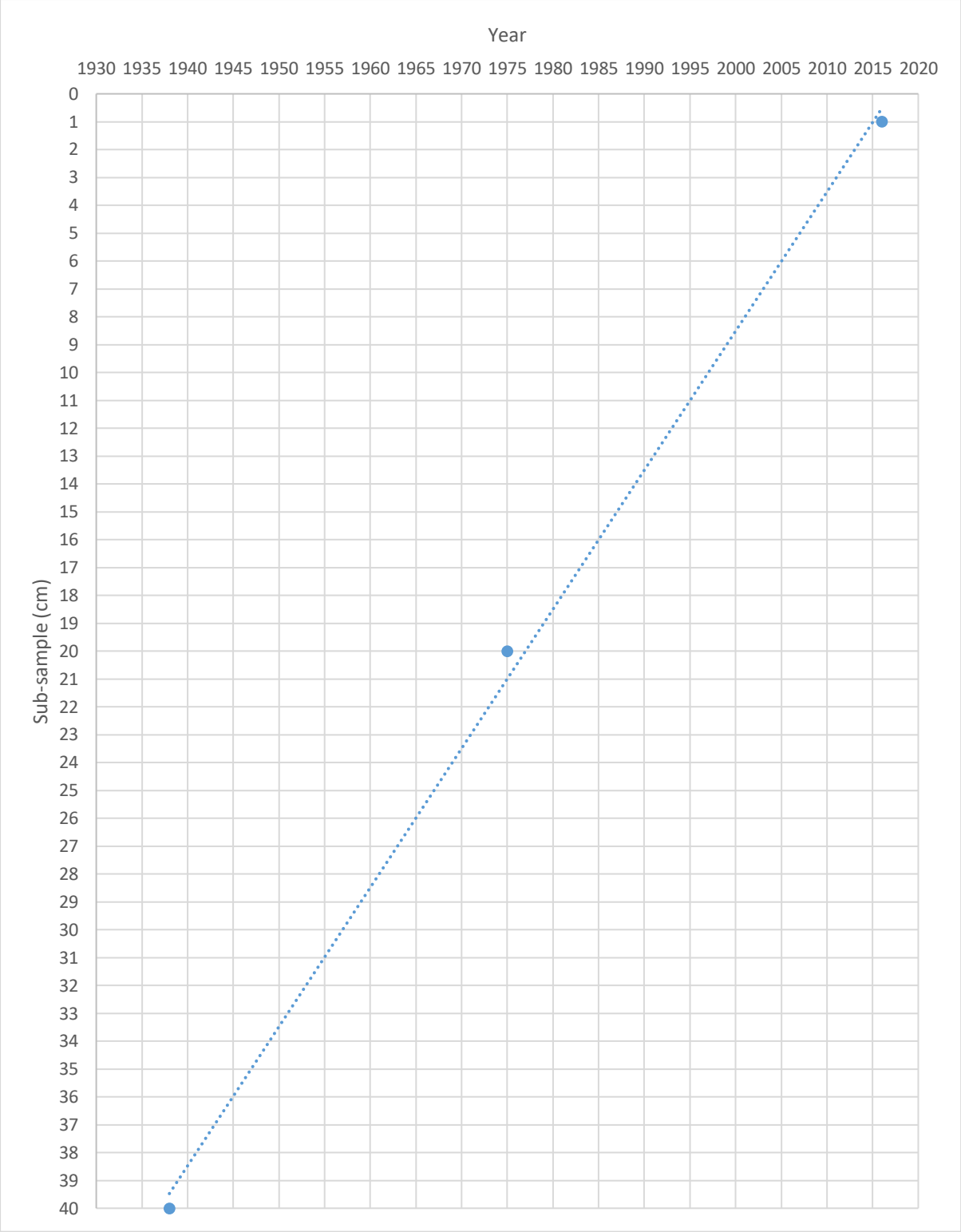

Fig. 16: Down-core profile of estimated dates based on average sedimentation rate of 0.47 cm/yr, ^{137}Cs peaks and the date the cores were extracted.

Microplastic Analysis

Below are the raw data tables for Core 1 and Core 2 showing the counts for each microplastic type, and the total counts of microplastics.

Core 1				
Sub-sample (cm)	**Pellets**	**Fibres**	**Fragments**	**Total MPs**
1	2	3	4	9
2	5	2	2	9
3	6	0	3	9
4	0	0	5	5
5	16	0	9	25
6	10	1	4	15
7	5	1	1	7
8	7	3	2	12
9	0	1	4	5
10	5	0	2	7
11	2	0	2	4
12	4	0	2	6
13	0	0	0	0
14	0	0	0	0
15	0	0	0	0
16	2	0	7	9
17	2	0	1	3
18	5	0	0	5
19	12	0	2	14
20	12	0	0	12
21	13	0	1	14
22	21	0	0	21
23	13	0	0	13
24	17	0	1	18
25	20	0	0	20
26	32	0	4	36
27	13	0	1	14
28	9	0	2	11
29	5	0	2	7
30	0	0	0	0
31	0	0	0	0
32	0	0	0	0
33	0	0	0	0
34	0	0	0	0
35	8	0	1	9
36	10	0	0	10
37	0	0	0	0
38	3	0	0	3
39	1	0	0	1
40	3	0	2	5
Total	263	11	64	338

Table 6: Raw data for particle counts, C1

Core 2				
Sub-sample (cm)	**Pellets**	**Fibres**	**Fragments**	**Total MPs**
1	0	0	0	0
2	2	0	0	2
3	1	0	0	1
4	8	1	2	11
5	5	0	0	5
6	2	0	0	2
7	6	2	0	8
8	5	0	1	16
9	6	1	1	8
10	8	0	5	13
11	7	0	3	10
12	9	0	0	9
13	4	0	2	6
14	2	0	1	3
15	3	1	0	4
16	8	0	0	8
17	5	0	3	8
18	12	0	2	14
19	12	1	0	13
20	11	0	3	14
21	11	1	0	12
22	16	0	1	17
23	15	0	1	16
24	10	0	2	12
25	10	0	0	10
26	16	4	3	23
27	19	0	1	20
28	6	0	3	9
29	9	0	1	10
30	3	0	2	5
31	5	0	1	6
32	7	0	1	8
33	0	0	1	1
34	2	0	0	2
35	0	0	0	0
36	2	0	1	3
37	2	0	0	2
38	0	0	0	0
39	0	2	0	2
40	1	0	1	2
Total	250	13	42	305

Table 7: Raw data for particle counts, C2

The down-core trend of microplastic pollution (Fig. 17 and Fig. 18) shows their presence even in the lower regions of the cores. The number of particles in both cores seems to stay relatively consistent throughout, with a slight decline towards the top of the cores. From 40 – 35 cm, both cores show low-level microplastic pollution (< 3 mps/cm^3). At around 33 cm (~ 1952), both cores begin a steady increase, peaking at 26 cm (~ 1966). The peak at 26 cm for both cores is almost entirely driven by pellets. Following this peak, there is a general decline in the number of particles found, with minor fluctuations. From 15 - 10cm, C2 sees a slight increase, whilst C1 declines further. At 5 cm (~ 2008), C1 sees another peak, before numbers fall again. C2 sees a similar pattern, however it is slightly lagged, and the numbers are lower. Both cores end at 0 cm with very few microplastic particles present.

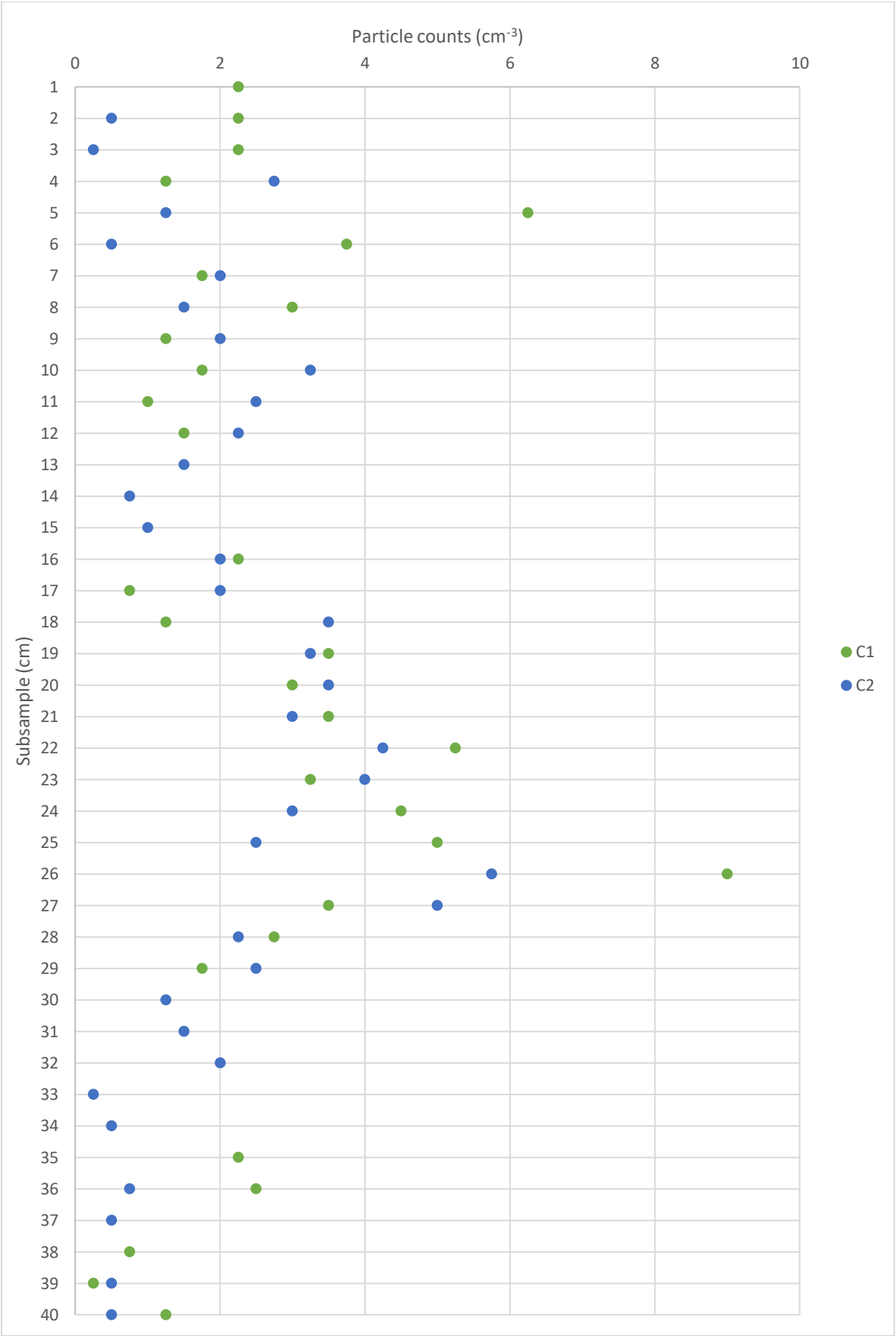

Fig. 17: Down-core profile measuring concentration of microplastic particles (cm^{-3})

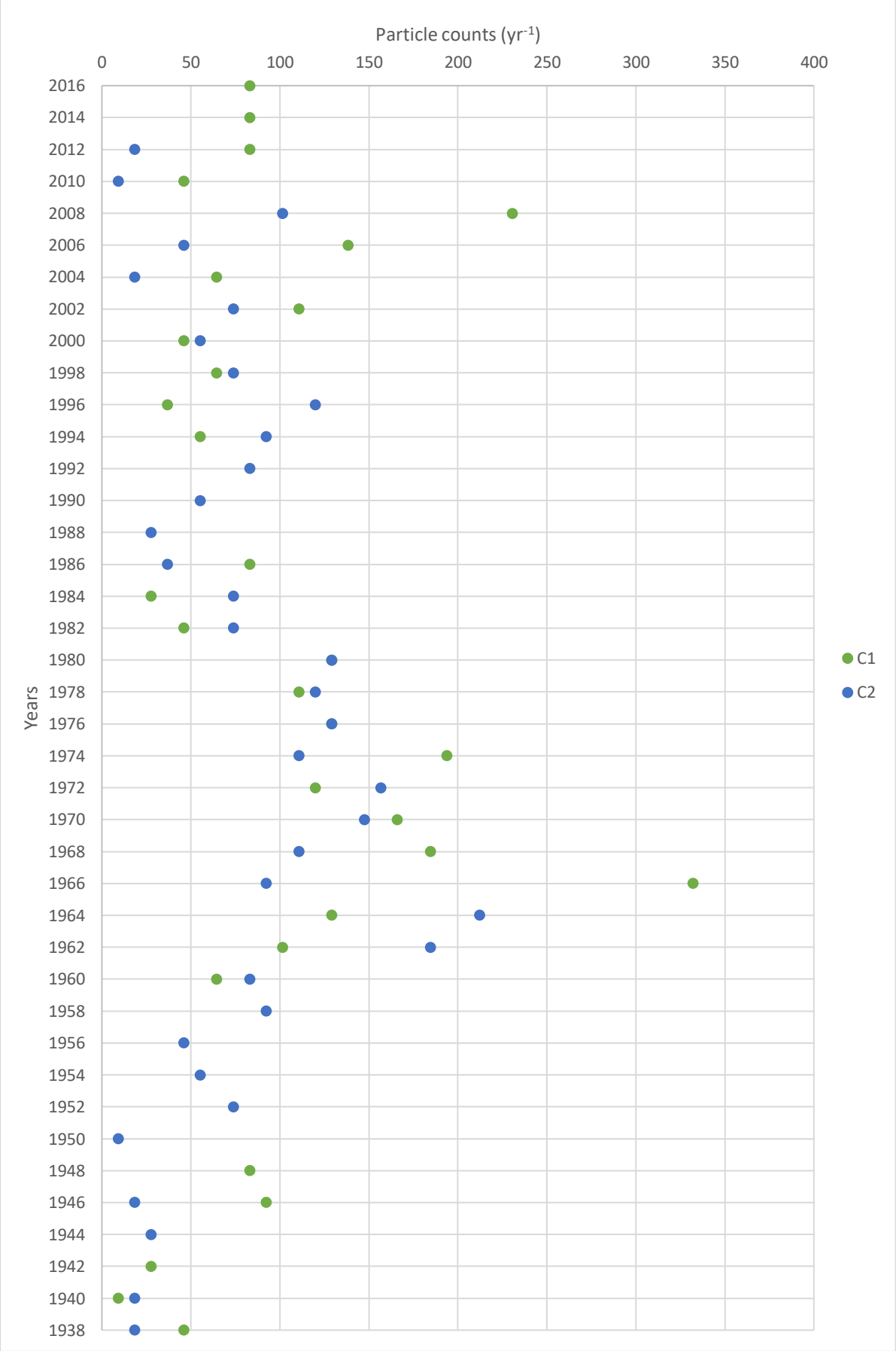

Fig.18: Down-core profile measuring accumulation rate of microplastic particles (yr^{-1})

The down-core trend of the types of microplastic particles highlights key peaks and may indicate the deposition characteristics of the different microplastic types. There is a strong, positive correlation between the number of particles found in C1 compared with C2 ($r_s(40)= 0.455$, $p= 0.003$). For C1 *(*Fig. 19*)*, fibres are exclusively present in the top 10 cm of the core, where particle size is much finer. Pellets are mostly found between 16-30 cm, where the sediment is predominantly coarse silts. Fragments show more presence in top 10 cm of the core, where particle size is made up mainly of fine to very fine silts. In C2 *(*Fig. 20), there does not seem to be a distinct pattern for any of the microplastic types, although there is an increase in pellets between 15-30 cm, which can also be seen in C1.

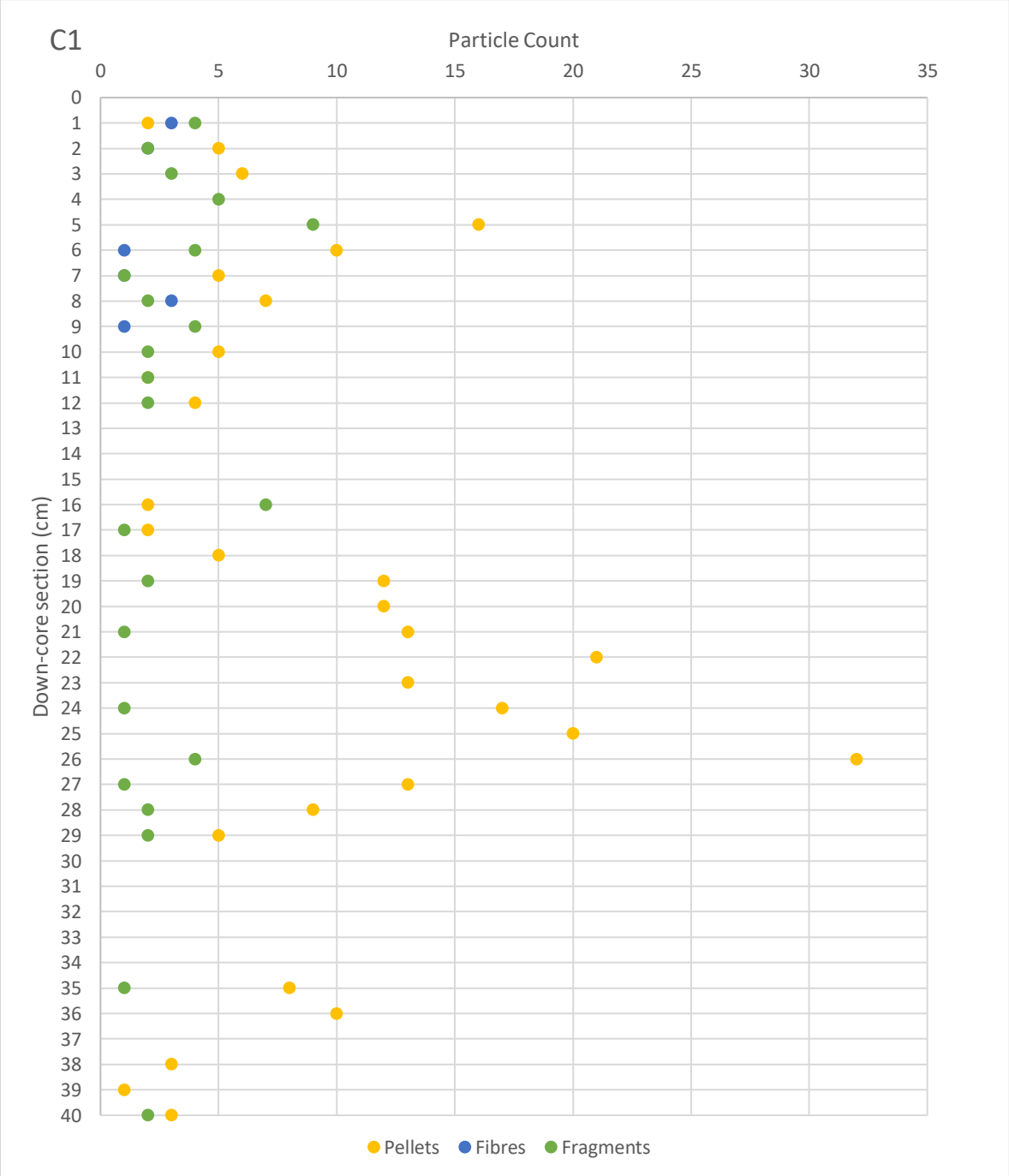

Fig. 19: Down-core profile showing concentration of each type of microplastic particle, C1

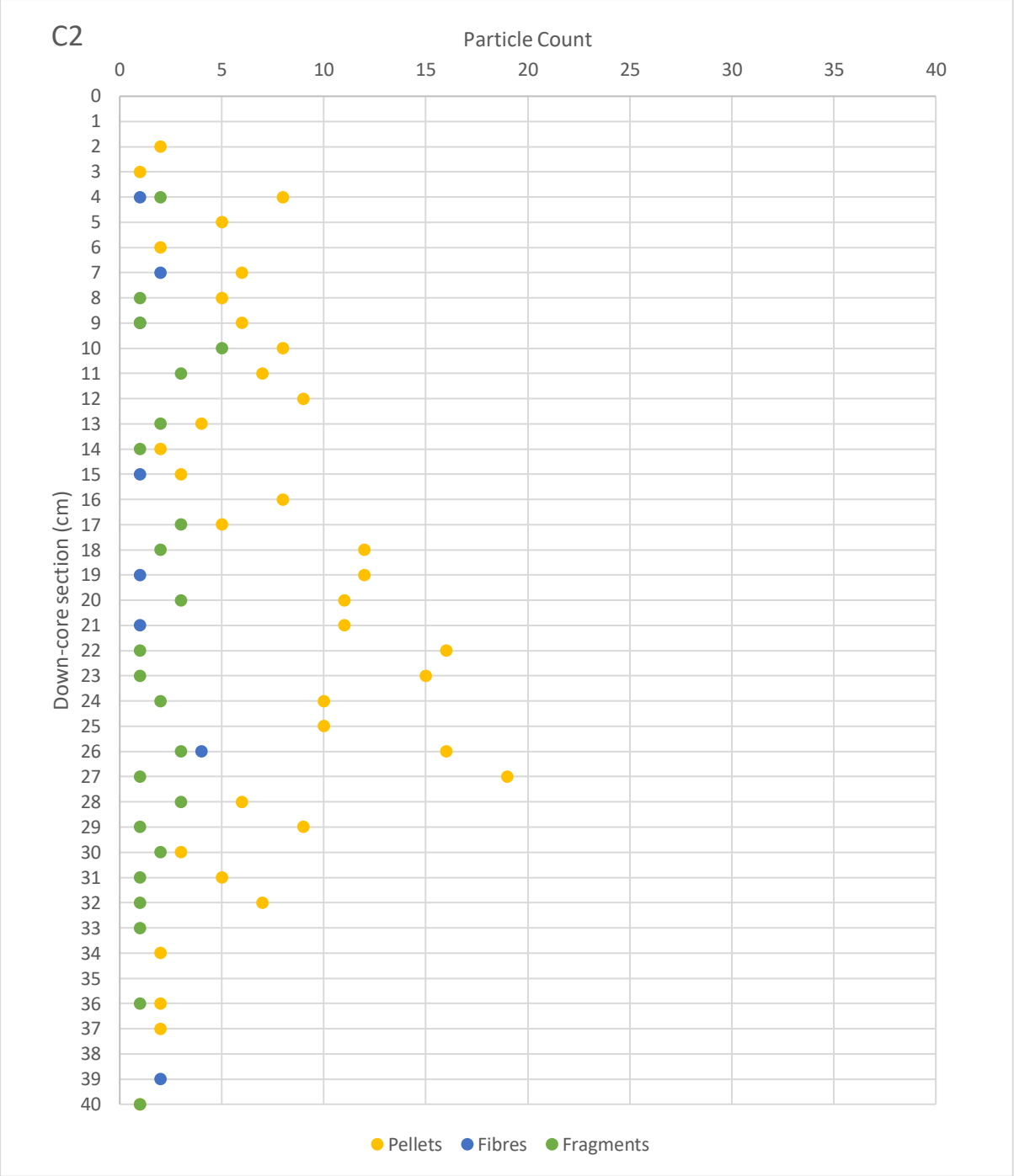

Fig. 20: Down-core profile showing concentration of each type of microplastic particle, C2

There is a strong, positive correlation between the number of pellets found in C1 compared to C2 (r_s (40) = 0.522, p= 0.001) (Fig. 21). There is a clear increase at 15 cm *(~1988)*, peaking at around 25-26 cm *(~1966)* before decreasing down to 30 cm *(~1958)*. The number of fibres (Fig. 22) in C1 is extremely low, and they are only found in the top 10 cm. In C2, very low numbers can also be seen, with no fibres found between 29 – 39 cm. Fragments (Fig. 23) remain relatively consistent throughout both cores, with an increase towards the top of C1, and a decrease towards the top for C2.

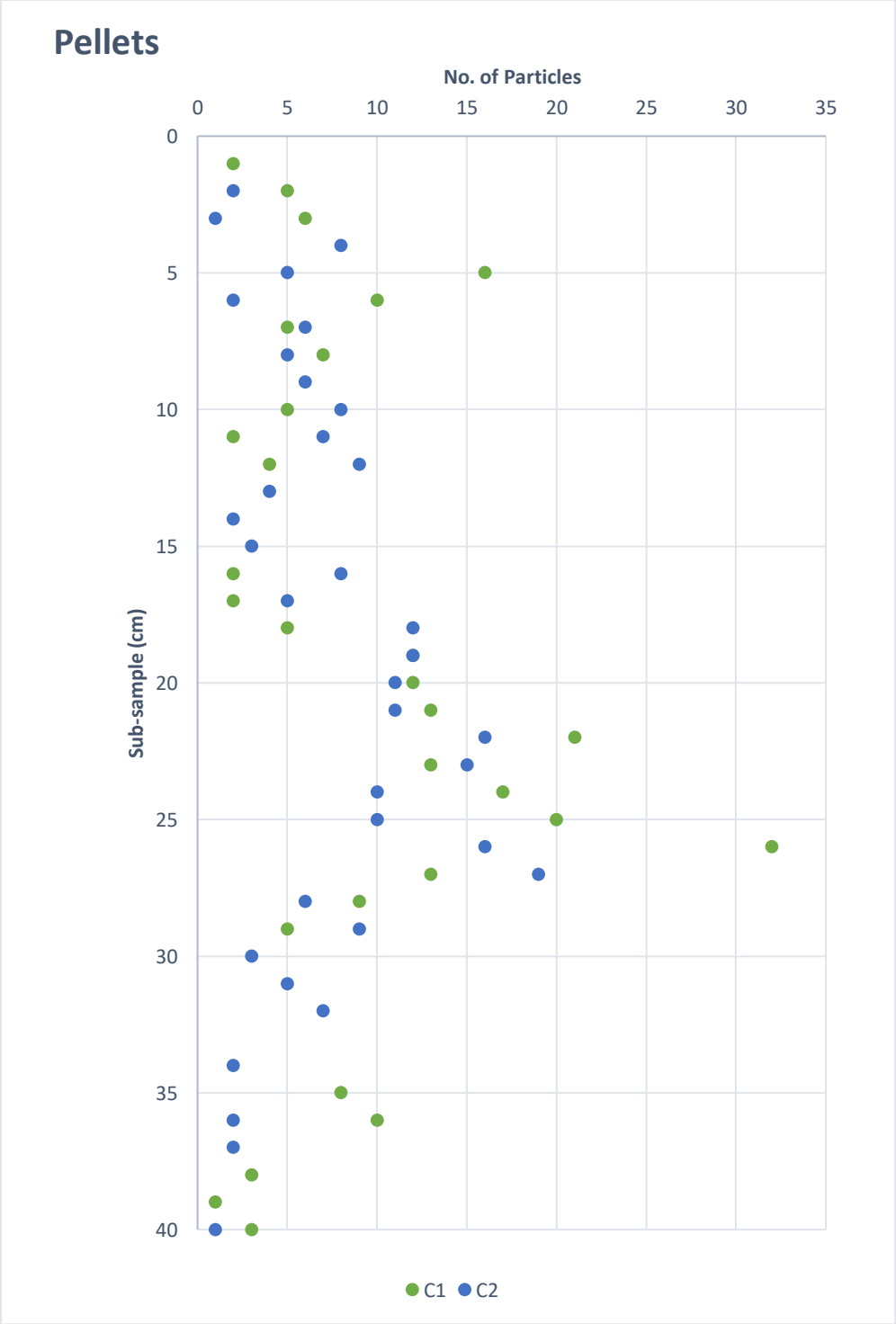

Fig. 21: Down-core profile showing concentration of plastic pellets for both cores

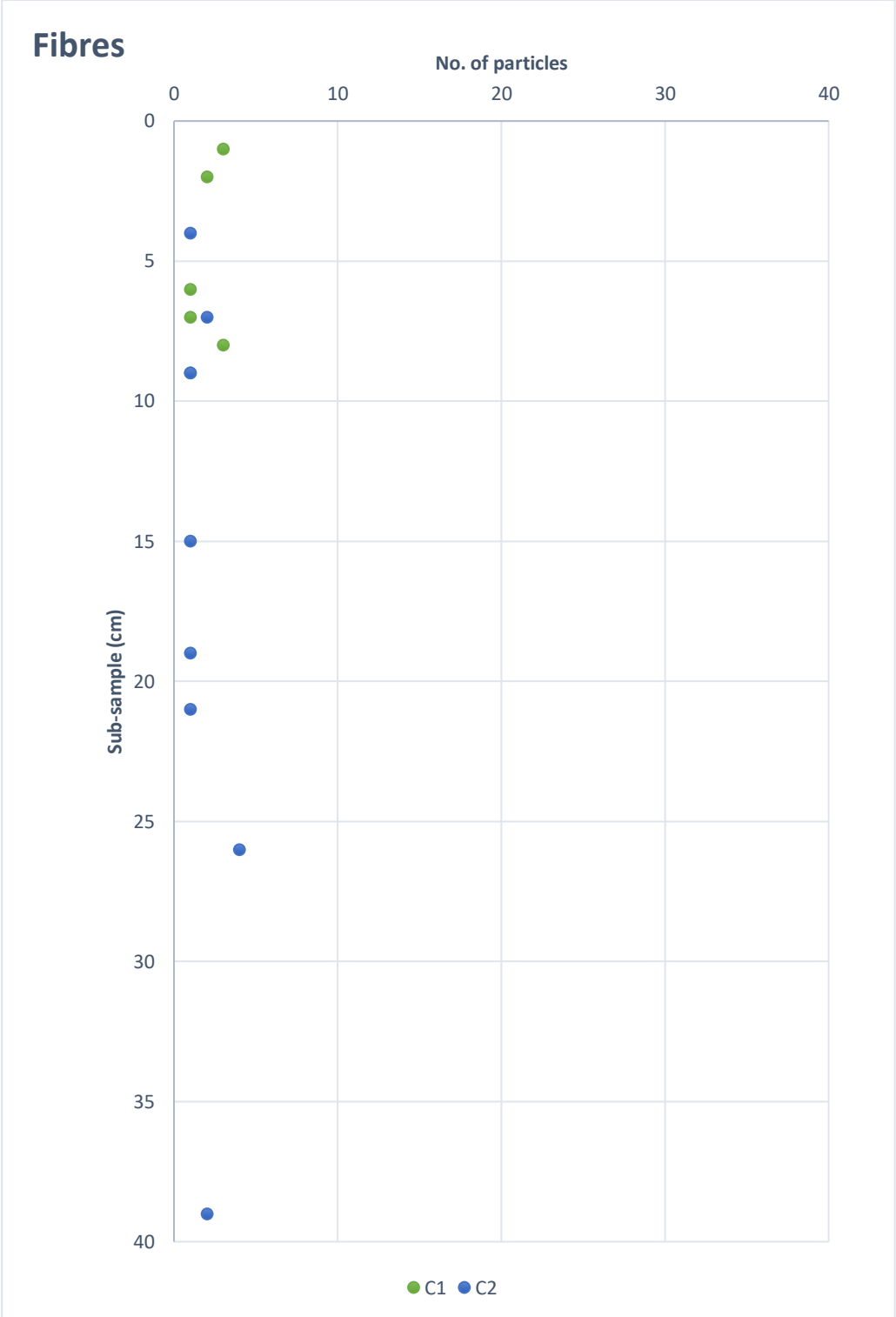

Fig. 22: Down-core profile showing concentration of plastic fibres for both cores

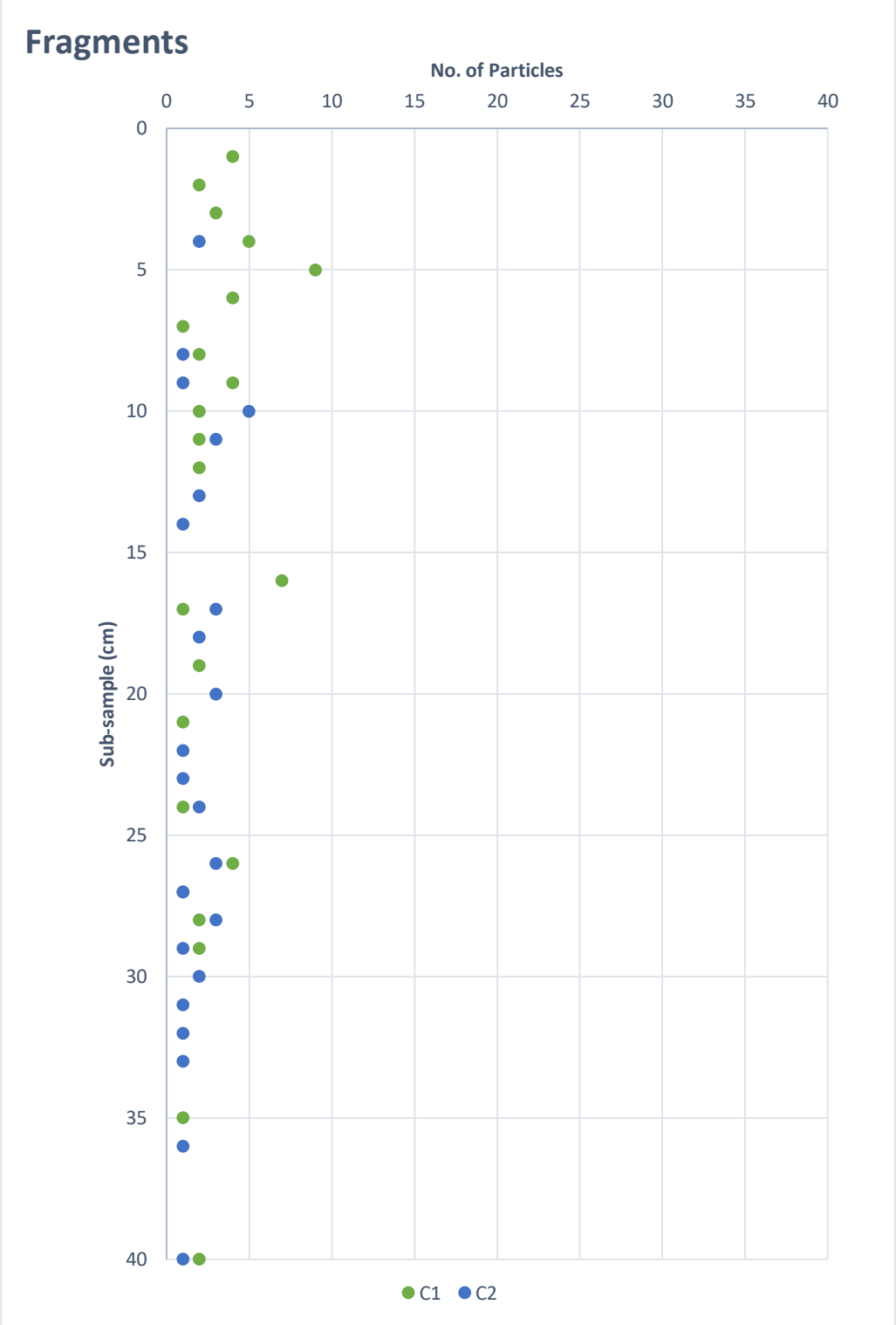

Fig. 23: Down-core profile showing concentration of plastic fragments for both cores

Although there is no significant correlation between mean grain size and microplastic concentration for C1 (r_s (40) = 0.154, p= 0.344), or C2 (r_s (40) = -0.148, p= 0.363), sub-samples with the highest amounts of plastic particles are mostly fine-grained. In C1, the amount of microplastic particles seem to increase as the grain size becomes finer (Fig. 24).

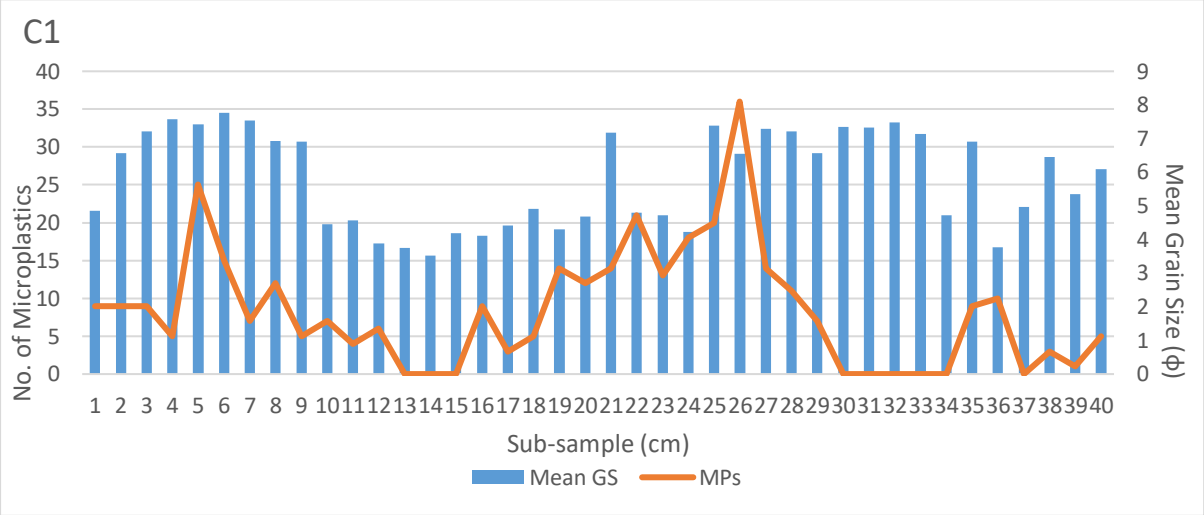

Fig. 24: Mean grain size (ϕ) vs. microplastics for C1.

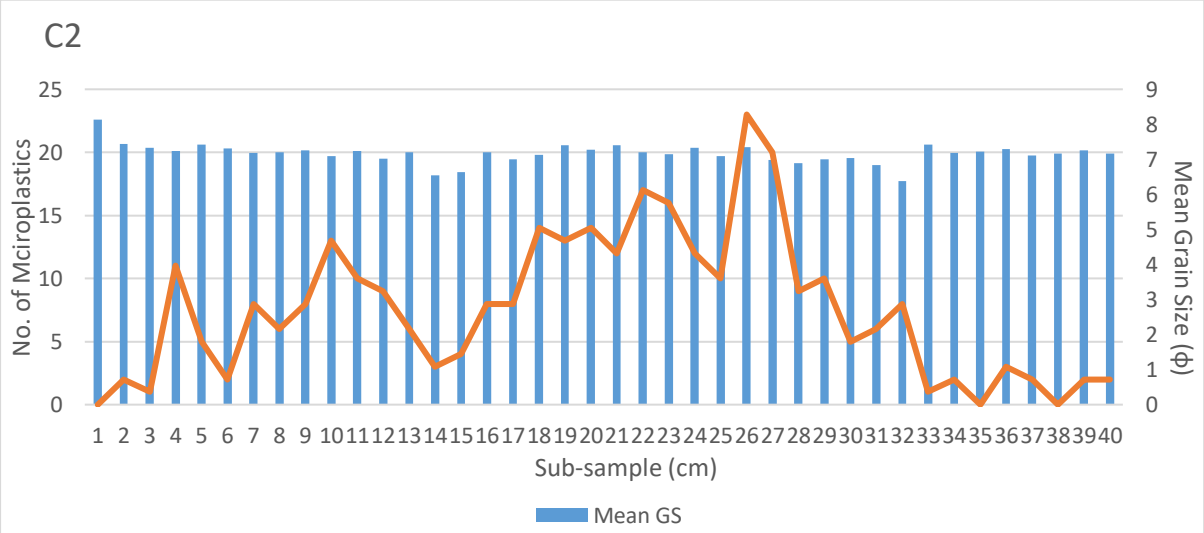

Fig. 25: Mean grain size (ϕ) vs. microplastics for C2.

Discussion

The two main aims of this study were to improve the extraction efficiency of microplastics from fine grained, organic rich sediments, and to examine how microplastic pollution has changed over time. Below, the methodological developments for the study are discussed, followed by a discussion on the spatial and temporal trends of microplastic pollution in relation to sedimentological parameters and the geochronology of the marsh.

Methodological Development

The method created for this study focused on the restricted use of harmful chemicals, whilst still attempting to reduce the amount of organic and inorganic material left on the filters. The use of hydrogen peroxide has been questioned in the past, as a high concentration H_2O_2 used over a long period can have adverse effects on the plastic particles themselves, which makes determining their origin almost impossible. Some studies report that digestion in a low concentration H_2O_2 for a period of 7 days or less does not cause damage to the plastic particles (Nuelle et al., 2014), but this only considers the most common polymer types. Instead of using a digestion step, which may influence the presence or appearance of plastic, a more rigorous sieving process was introduced, in the hope that this would greatly reduce the amount of silts, clays and organic matter present in the samples. For this step, microfiltration was chosen as the best technique to reduce the amount of very fine grains, based on its previous uses in separating pollen grains from substrates (Montes-R and White, 1995). A 1 mm sieve was first used to remove larger material, followed by a 6 µm mesh to filter out smaller particles, which gave the size fractions necessary for this study.

Density separation is the most common method used to extract lighter plastic particles from heavier grains. Saline solutions such as sodium chrloride (NaCl) are often used to float off the lighter particles (Hidalgo-Ruz et al., 2012). However, in this study, a high-density chemical was needed due to the organic rich nature of the sediment samples. Sodium Polytungstate (SPT) was chosen as the best solution to use because of its high-density nature and non-toxicity, and ability to extract a wider range of polymers (Klein et al., 2018, Peng et al., 2017). As well as this, SPT could be recycled and reused throughout the process, which made the method more cost effective and environmentally sustainable. Four separate density ranges were used to effectively extract a wide range of microplastics based on polymer densities, whilst reducing and separating the concentration of organic matter. A density range of 1.8 – 1.6 g cm^{-3} was used in the hope that most of the heavier organic matter would remain in this section (Christensen, 1992). The difference in density can be used to separate the lighter microplastics from these heavier particles (Rocha-Santos and Duarte, 2015).

Lighter sediments such as silt generally have densities of around 1.4 – 1.6 g cm^{-3} (Daddow and Warrington, 1983), hence using the density range of 1.6 – 1.4 g cm^{-3} to extract light sediments and organic matter as well as some heavier plastic particles. It was hypothesised that most microplastics would be extracted in the density ranges of 1.4 – 1.2 g cm^{-3} and ≤ 1.2 g cm^{-3}, as most common polymers have densities between these ranges (Table 3). Blank samples reported the presence of plastic fibres at each density range, which are likely to have originated from contamination of equipment, clothing, and airborne dust. No other types of particles were found in the blank samples, which suggests that those found in the cores originated from the marsh samples.

46 % of plastic particles were extracted at a density range of 1.6 – 1.4 g cm^{-3}. According to Table 3, the densities of the most common plastic polymers range from ~ 0.9 g cm^{-3} – 1.6 g cm^{-3}, with most polymers being in the lower range. Plastic pellets dominated both cores, making up 80 % of the total microplastic count. The polymer types of plastic pellets are generally PE and PP, which both have densities < 1 g cm^{-3}, however, figure 6 shows that 49 % of pellets came out at 1.6- 1.4 g cm^{-3}. Polymer density values often refer to the virgin resins, and do not take into account the effect various additives that are added during production may have on the polymer density (Hidalgo-Ruz et al., 2012). Moreover, once out in the environment, plastics will undergo weathering which may decrease the density of microplastics, and biological processes such as biofouling, which is known to increase the effective density of floating microplastics (Jahnke et al., 2017). Biofouling causes plastic debris with a density lower than that of seawater to sink and eventually deposit on the seabed. Particles formed by weathering processes may also aggregate with phytoplankton and natural inorganic particles such as clays that have higher sedimentation rates (Jahnke et al., 2017). Both cores were comprised mainly of fine to very fine silts with some clays present, suggesting that some of the microplastics found may have originated from marine sources, and have aggregated with particles that have higher sedimentation rates causing them to be deposited on the marsh. 67 % of fibres were extracted at 1.2 g cm^{-3}. According to Table 1, fibres mainly originate from fishing gear, plastic bags and clothing, and are likely to be made of LDPE (0.917 – 0.965 g cm^{-3}) or PP (0.9 – 0.91 g cm^{-3}). It is therefore likely that fibres extracted at the lowest density comprise of LDPE and PP polymers. It is possible that fibres extracted between 1.4 – 1.2 g cm^{-3} and 1.6 – 1.4 g cm^{-3} are comprised of PET (1.37 – 1.45 g cm^{-3}) and PES (1.24 – 2.3). Fibres that came out at 1.8 – 1.6 g cm^{-3} may also have aggregated with heavier organic matter causing them to be extracted at a higher density range. Very few fragments were extracted at density ranges of 1.8 – 1.6 g cm^{-3} and 1.2 g cm^{-3}, with the majority separating between 1.4 – 1.2 g cm^{-3} and 1.6 – 1.4 g cm^{-3}. Possible polymer types for these fragments include PET (1.37 – 1.45 g cm^{-3}), PVC (1.16 – 1.58) and POM (1.41 – 1.61). These are all strong polymers and have a wide range of

applications, from construction and automotive, to food packaging and drinking bottles (Plastics Europe, 2019).

Microplastic pollution on Biggar Marsh, Walney Island

It has been suggested that estuarine environments such as saltmarshes are likely to be a sink for microplastic pollution, as they are often primary locations for shipping and industrial development, and act as major transport pathways for many pollutants from terrestrial environments out to sea (Anderson et al., 2018). Both cores extracted from Biggar marsh on Walney Island were near a small residential area, which increases the likelihood of plastic litter entering the marsh from sources such as direct deposition and improper waste disposal, via pathways such as wind and runoff (Frias et al., 2014). The island is exposed to dominant westerly winds, which may transport litter from the Irish Sea onto the marsh, and could carry litter from the nearby residential and industrial areas, resulting in the breakdown of larger plastic debris into secondary microplastics such as microplastic fragments. In recent research, car tyres have been found to emit a significant amount of microplastics into the environment (Kole et al., 2017). Carr lane runs along the western side of the marsh, and is one of the main roads connecting the village of Vickerstown to the village of Biggar, suggesting it is a well-used road and is therefore a likely source of microplastics onto the marsh. Baugh (2019) measured the elevation of the marsh, and found that the high marsh slopes down into the middle marsh, falling slightly from 5.42 m to 5.09 m over 12 m. The elevation continued to gradually decline into the middle marsh, falling from 5.09 m to 4.63 over ~68 m. Heavy rainfall and extreme weather events may act as a pathway for both primary and secondary microplastics, from household waste and general litter, to the marsh. Heavy rainfall can also influence the distribution of sediment and debris, transporting newly deposited sediment from higher areas out onto the middle marsh, where this can enter creeks (Boorman, 2003).

The presence of several wastewater and sewage treatment companies near to Walney Island will also act as a source of microplastic pollution onto the marsh. The United Utilities WWTW in Broughton-in-Furness is located ~17 m north of the Island, next to a catchment that runs into the Irish Sea. Another is located in Ulverston, ~13 m northeast of the Island, situated next to the River Leven, which runs directly into Morecambe Bay. There is also a United Utilities WWTW located ~5 miles northeast of the Island, on the west coast of Morecambe Bay, and to the east of the Island is the Lancaster WWTW, where effluent may enter the River Lune. The Sowerby Woods industrial estate is located ~4 m north of the Island, and is home to several businesses such as SUEZ; a waste management service dealing in recycling and recovery, Oil States MCS Ltd; an oil and gas exploration service, and Furness Plastics; a sign-writer and manufacturer. These are all potential sources of primary microplastics onto the marsh, via pathways such as run off and effluent entering nearby rivers, transporting plastics out to

Morecambe Bay and beyond. Microplastics present in the water-column are likely to accumulate on the marsh as a result of tidal processes. These are the main influencing factors on sediment accretion and redistribution on the marsh (Christiansen et al., 2000), and are therefore one of the main pathways for microplastic pollution. Morecambe bay has a large everyday spring tidal range of ~8.2 m, with the Mean High-Water Springs (MHWS) being 4.6 m and Mean Low-Water Springs (MLWS) being 3.6 m (Mason et al., 1999). The average water flow is northwards from St. Georges Bay to the North Channel (Barne et al., 1996), suggesting debris from coastal areas along this route may deposit further up.

Most pellets were extracted between 1.6 g - 1.4 g cm^{-3} (Fig. 11), which suggests that their density has likely increased, as polymers that are usually associated with this type of microplastic are Polyethylene (PE) and Polypropylene (PP), which both have densities < 1 g cm^{-3}. Kaiser et al (2017) reported that the presence of low density microplastics in nearshore subtidal sediments strongly suggest that a proportion of floating microplastics remain at sea long enough for biofouling to cause sinking. Biofouling is common in marine environments such as coastal waters (Kaiser et al., 2017, Frère et al., 2017), and can affect the sinking rate of plastic debris by altering the density of the particle. This process essentially reduces the amount of degradation whilst at the same time increases the density of the particle, as plastics will likely sink and become buried, which subsequently reduces the amount of UV radiation reaching the surface of the plastic (Weinstein et al., 2016). Microplastics are then more likely to be transported onto the marsh within the suspension load, when the flow of water onto the marsh is enough to maintain fine particle sizes, and as the flow velocity decreases, the finer particles will gradually settle to the bed, enhanced by flocculation (Rahman and Plater, 2014). This would suggest that microplastics are more likely to deposit within fine-grained sediments.

Grain size data was collected for both cores in order to identify any links between the presence of microplastic pollution and the depositional characteristics of the marsh. There was a significant difference ($U_{40, 40}$ = 417.5, p= 0.000) between the mean grain size in C1 compared to C2, despite the cores being situated in the same marsh zone, approximately 48 m apart. There were no significant differences, however, between the sorting, skewness and kurtosis in either cores. The significant difference between the mean grain size of the cores is due to the presence of coarser grain sizes between 10 – 24 cm in C1. In Fig. 6, 7, 8 and 9, the grains in C1 become coarser, very fine skewed and very leptokurtic, and moderate to poorly sort, compared to the rest of the core which is very fine grained, poorly to very poorly sort, platykurtic and fine skewed. Coarse grains are associated with high energy conditions (de Groot et al., 2011), so during this period of sediment accretion it is likely that the marsh experienced changes in tidal flow deposition, from the suspension load that settles during the turn of the tide (‘slow tide’) to the traction load deposited by faster tidal flow velocities (‘fast tide’)

(Rahman and Plater, 2014). Coarse grains are more likely to be deposited in this area due to the increased vegetation cover, which causes a dampening effect and increases the likelihood of larger grain sizes present in the water column being deposited (Baugh, 2019, Möller and Spencer, 2002). C2 does not seem to be affected by the change in tidal flow deposition, and displays a consistent mean grain size throughout, indicative of 'slow tide' deposition found in upper to mid saltmarsh environments (Rahman and Plater, 2014). The presence of a creek system ~40 feet away from C2, and the reduced vegetation cover, may also have an effect on the depositional characteristics in this area. Studies have noted that rates of sediment deposition are often controlled by the proximity to creeks (French et al., 1995), with some noticing a decline in sediment deposition away from the creeks (Reed et al., 1999).

There was no correlation between the number of microplastics found in the cores and mean grain size, suggesting this does not have an influence on the deposition of microplastic particles over this particular area of the marsh. However, Fig. 24 does seem to show some relationship between fine grains and the presence of microplastics. Browne et al (2010) also reported no clear relationship between microplastics and fine grains, but explained that these types of sediments are cohesive and regularly flocculate with organic material, which may contribute to movements of microplastics in the water-column. However, Daddow and Warrington (1992) explain that soils with large amounts of fine particles such as silts and clays will have smaller pore diameters and higher penetration restrictions. This could explain why there are slightly less particles in C2, as the grain size here is made up of very fine silts (Fig. 6) and there is no variation throughout, unlike C1, which shows slight changes in the mean grain size and sorting. Further to this, a strong significant positive correlation was found between the sorting of the grains and the number of pellets in C1 (r_s (40) = 0.840, p = 0.033), and a significant positive correlation was found between the sorting of the grains and the number of fibres in C1 (r_s (40) = 0.342, p = 0.031). Clearly, the sorting in C1 has a significant impact on the likelihood of microplastics depositing in this area of the marsh, although no significant differences were found in the sorting of the grains for both cores. When comparing Fig. 6, 7, 8 and 9 with the temporal trends in microplastic concentration in Fig. 17, it is evident that the shift from 'slow tide' to 'fast tide' resulted in an increase in microplastics being deposited on the marsh during this time.

There was no significant difference in the concentration of microplastic pollution in C1 compared with C2 ($U_{40, 40}$ = 797, p= 0.977), most likely due to the proximity of the cores. This suggests the sources of microplastics onto the marsh are the same in this area. As well as this, no significant differences were found in the number of pellets, fibres or fragments found in C1 and C2, suggesting the depositional dynamics in this area of the marsh are likely to be similar. Both cores were taken from the middle marsh area, defined by a diverse range of vegetation species, from *Puccinellia sp.,* to *Triglochin*

maritima (Baugh, 2019), as well as the presence of creeks and a more frequent inundation of tidal waters. Pellets make up 80 % of the total count for both cores, suggesting saltmarshes are likely to be a sink for this type of microplastic pollution. As well as this, a strong positive correlation was found between pellets in C1 and C2, suggesting the variables determining the deposition of these particles are the same for both areas, and again points to a similar point of origin. Microplastic pellets are mostly associated with industrial and cosmetic use; therefore, the presence of several wastewater treatment works and industrial parks around Walney Island is undoubtedly affecting the amount of microplastic pollution in the area. Due to their microscopic size, microplastics such as pellets coming into sewage and wastewater treatment works from household waste are not always captured or filtered out (Fendall and Sewell, 2009, Browne et al., 2011). Consequently, it is likely that microplastic pellets depositing on the marsh are originating from these sewage and wastewater treatment works and are transported to the marsh via effluent that has been discharged into nearby rivers. As well as this, microplastics are likely to be incorporated into sludge waste from sewage treatment works, which may be applied to agricultural land. Much of the area around Walney Island is used for agriculture, so it is therefore likely that microplastics incorporated in this sludge could be deposited on the marsh via terrestrial runoff entering nearby rivers.

Fragments made up 16 % of the total microplastic count. These are secondary microplastics, associated with the fragmentation of larger plastic debris. Most of the fragments found in the cores were extracted between 1.4 – 1.2 g cm^{-3} and 1.6 – 1.4 g cm^{-3}, and are likely to be made of PET, PVC or POM, which are all strong polymers associated with a wide range of applications, from construction and automotive, to food packaging and drinking bottles (Plastics Europe, 2019). These microplastic fragments will be depositing on the marsh most likely from direct deposition of plastic litter, which is then broken down over time. Fibres made up only 4 % of the total microplastic count, despite the fact that they are mainly associated with synthetic clothing and will be incorporated into effluent and sludge discharged from sewage and wastewater treatment works. The majority of microplastic fibres (67 %) were extracted at the lightest density of 1.2 g cm^{-3}, and are most likely made from LDPE or PE associated with clothing, fishing gear and plastic bags. Due to their lightweight nature, it is probable that these microplastics are less likely to be deposited on the marsh and are more likely to remain in the water-column or be transported away via wind and currents. However, fibres are still prone to biofouling, which may account for the small numbers extracted at higher density ranges.

The temporal record of microplastic accumulation observed in both cores taken from Biggar marsh does seem to follow the historical increase in global plastic production. When comparing microplastic concentrations in the cores to the crude geochronology of the cores (Fig. 15), the results show that 40 – 35 cm relates to the years 1938- 1948. The major growth point of the plastics industry was from

1930. During the years between 1930 and 1940, four major thermoplastics were developed; Polystyrene (PS), Polyvinyl chloride (PVC), the polyolefins, and PMMA (Gilbert, 2017). According to Gilbert (2017), the years between 1940 and 1950 saw the rapid discovery and development of many new plastic polymers. This decade saw the development of new thermoplastics, such as HDPE and PP (Gilbert, 2017), which are among the most common polymers used today, and are the main polymers used for creating plastic pellets (Frias et al., 2010). A general increase in microplastics found on the marsh during this time can be seen, until around 26 cm where the number of microplastics peaks. According to the crude geochronology of the cores, this peak should have occurred around 1966, when the development of new plastics was still ongoing, and commercial use was ever increasing (Gilbert, 2017). There is a distinct increase in plastic pellets between 30 – 15 cm for both cores (Fig. 18), which spans over approximately 30 years, from ~1958 to ~1988. Plastic pellets or 'nurdles' are commonly made from Polyethylene (PE) which was used commercially in the UK from 1939, and Polypropylene (PP) which was first produced in 1957 (BPF, 2014), which could explain the peak in plastic pellets found in the cores during this time. According to Perschbacher (2016), the use of microbeads in personal care products began in the late 1960s, however they were not used commercially until the 1990's.

The overall decrease in microplastics from ~18 cm, which when compared to the age model is around the early 1980's, could be explained by the development of waste management in the UK, especially the recycling of materials such as tin, paper and plastic (Rubbish Please, 2018). Cole et al (2011) explains that in the past, marine vessels have been a major contributor to marine litter, and it is estimated that during the 1970's the global commercial fishing fleet discarded over 23,000 tons of plastic packaging materials. In 1988, an international agreement was employed banning marine vessels from dumping plastic waste at sea. Gilbert (2017) reports that although there has been a steady increase in plastic consumption globally, the growth of plastic consumption in Europe seems to have slowed. The general decrease in microplastics seen in Fig. 17 may be following the annual average growth rate of plastics, which had previously been 15 % prior to the oil crises in the 1970's, but dropped to 8 % after this period, from 1974 to 2005 (Gilbert, 2017). This decline in growth rate of plastics coupled with the introduction of better waste management in the UK is evident in the microplastic particle counts seen in Fig. 17 for both cores.

It is possible that peaks in microplastic concentrations for the cores are driven by factors associated with changes in climate and weather patterns, such as increased storm events (Yonkos et al., 2014) and sea level rise, rather than increases in plastic production over time. Sea level rise has the ability to increase sediment availability in coastal systems, ultimately resulting in a more active system with increases in water depth and wave height (Boorman, 2003). In both cores, pellets and fragments were generally found throughout the entire core; however, the presence of fibres is much scarcer. In C2,

fibres are not generally present until ~26 cm, with the exception of two fibres found at 39 cm. This could be explained by increased popularity of synthetic clothing during the 1960's and 70's. In C1 however, fibres can only be found in the top 10 cm. The amount of energy needed to transport fibres is low enough for them to travel to the lower regions of the middle marsh but has not quite been enough to transport them any higher. However, in a report on the climate of the UK and recent trends, it is stated that the rate of relative sea level rise around the UK in the 1990s and 2000s is higher than that for the 20th century overall (Jenkins et al., 2009). It is therefore likely that due to recent sea level rise and consequent increased tidal range, fibres have only recently been deposited this high up on the marsh.

The North West of England receives extremely high rainfall and is prone to extreme weather events such as storms and flooding. Heavy rainfall is known to increase suspended sediment concentrations in tidal waters (Voulgaris and Meyers, 2004), allowing any microplastic particles present in the water-column to become flocculated with fine grains, increasing the likelihood of them sinking and depositing once the tidal flow has slowed down. There is a clear shift in depositional characteristics between 24 – 10 cm, indicating a change in tidal flow most likely linked to changes in weather patterns, affecting sediment flow into the marsh. The peaks at 26 cm and 5 cm seem to occur either side of this shift, suggesting these weather events increased the likelihood of microplastics depositing on the marsh. The general decline in concentrations of microplastic particles seen in both cores, from ~26 - 0 cm, could not only relate to the introduction of stricter waste management policies, but could also be an outcome of reduced sediment accretion on the marsh. It is possible that sediment accretion has slowed down in recent years, similar to the Dee estuary (Hutchinson and Prandle, 1994), therefore less microplastic particles are being transported within the sediment load. Mason et al (1999) reported a net loss of approximately 16 x $10^6 m^3$ of sediment over the period 1992 – 1997 from the intertidal region of Morecambe Bay, as a result of losses between mean sea level and the low-water mark. These changes were also seen in the main river estuaries within the bay; the Leven, Kent and Lune (Mason et al., 1999).

Conclusion

Despite the majority of plastic litter being produced on or near the shore (Thompson, 2017), there has been very little investigation into the accumulation of microplastic pollution in depositional environments such as saltmarshes. These ecosystems act as transitional pathways for pollutants from terrestrial to marine environments and are therefore prone to microplastic pollution from both of these sources. However, due to their organic rich nature, the extraction of microplastics from these sediments is extremely difficult, and a standardised method does not exist. The aims of this study were to improve the extraction efficiency of microplastics from fine grained, organic rich sediments, and to examine how microplastic pollution has changed over time.

The results have established microplastic pollution on Biggar marsh, and the method developed has proven to efficiently extract microplastics from these sediments. The density range of 1.8 – 1.6 g cm^{-3} successfully removed large amounts of organic matter from the samples, reducing the amount found in subsequent density ranges. The majority of plastics (46 %) were extracted between 1.6 – 1.4 g cm^{-3}, despite most common polymers being ≤ 1.2 g cm^{-3}. Plastic pellets were dominant in both cores, making up 80 % of the total proportion, suggesting that saltmarsh ecosystems are a likely sink for this type of pollution. Blank samples contained low concentrations of fibres in each density range, with no contamination from pellets or fragments reported.

The presence of several sewage and wastewater treatment works near to Walney Island has undoubtedly led to microplastic pollution on the marsh, via the discharge of effluent into nearby rivers and eventually out into Morecambe Bay and beyond. Other sources resulting in microplastic pollution on the marsh include a high concentration of industrial, manufacturing and shipping development near to the marsh, fibres from eroding car tyres, and the breaking down of larger plastic debris deposited directly onto the marsh, such as bottles and fishing gear. The use of sludge on nearby agricultural land is also a likely source of plastic pollution, entering river systems via runoff.

No correlation was found between microplastic concentrations and mean grain size, suggesting particle size does not influence microplastic deposition, however, positive correlations were found between the sediment sorting and the number of pellets and fibres in C1, suggesting that areas of the marsh showing more variability in the sorting of grains are more likely to harbour microplastics.

Due to the dynamic nature of the marsh and the complex depositional characteristics, it is difficult to determine whether the presence of microplastic pollution on the marsh is more influenced by changing in sediment availability or trends in global plastic production. The record of microplastics accumulation observed in both cores taken from Biggar marsh does seem follow the growing historical

increase in global plastic production, but is clearly influenced by sediment accretion patterns and weather events on the marsh.

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